Low-Cost Diffusion Samplers for VOCs in Groundwater

By Don A. Vroblesky

U.S. Geological Survey

Outline

Diffusion Samplers

- Theory (Principles of Operation or Effectiveness)
- Applicability
- Cost
- Regulatory Issues
- Case Histories
- Advantages and Limitations
- Summary and Conclusions
- References
- Information Sources and Tech Transfer Tools

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Conventional Well Sampling Methods

Two standard methods

- Purge-and-Sample
  - Remove 3 or more casing volumes of water prior to collecting a sample
- Low-Flow (LF) or Low-Volume Sampling
  - Slowly purge until field parameters stabilize prior to collecting a sample

Principle

Diffusion Samplers

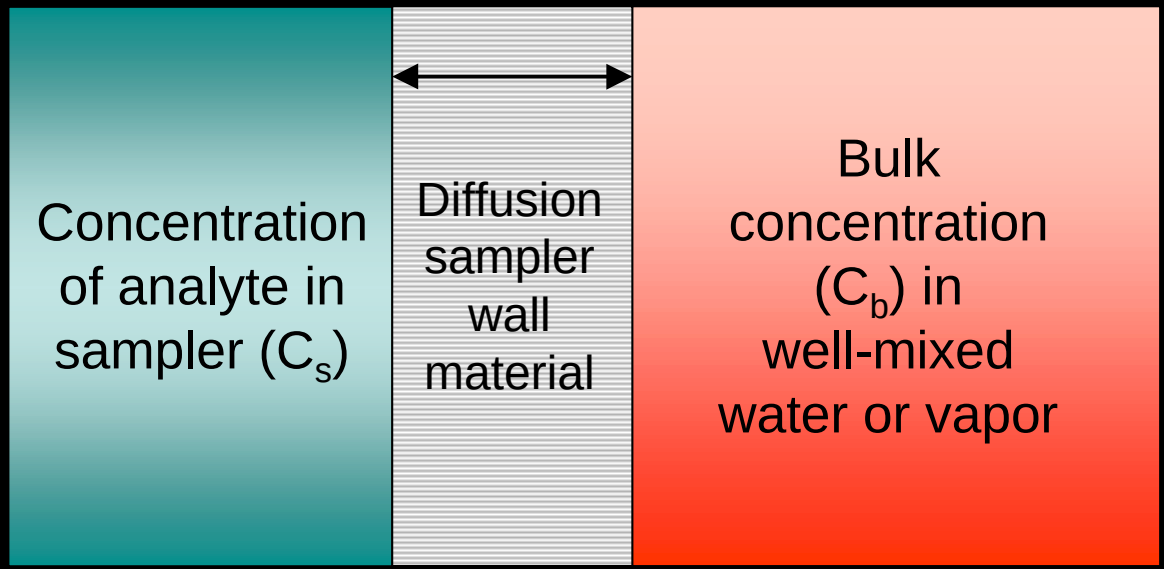
- **Law of Diffusion**
  - Compounds tend to migrate from an area of high concentration to an area of low concentration until equilibrium is achieved

- **Fick's Law**
  - The rate of diffusive mass transfer through a unit area (flux or J) is proportional to the difference in concentrations divided by the distance separating those concentrations. The constant of proportionality is also called the diffusivity, or diffusion coefficient (D).

Fick's Law: $$J = \frac{D}{L}\left(C_b - C_s\right)$$

Principle

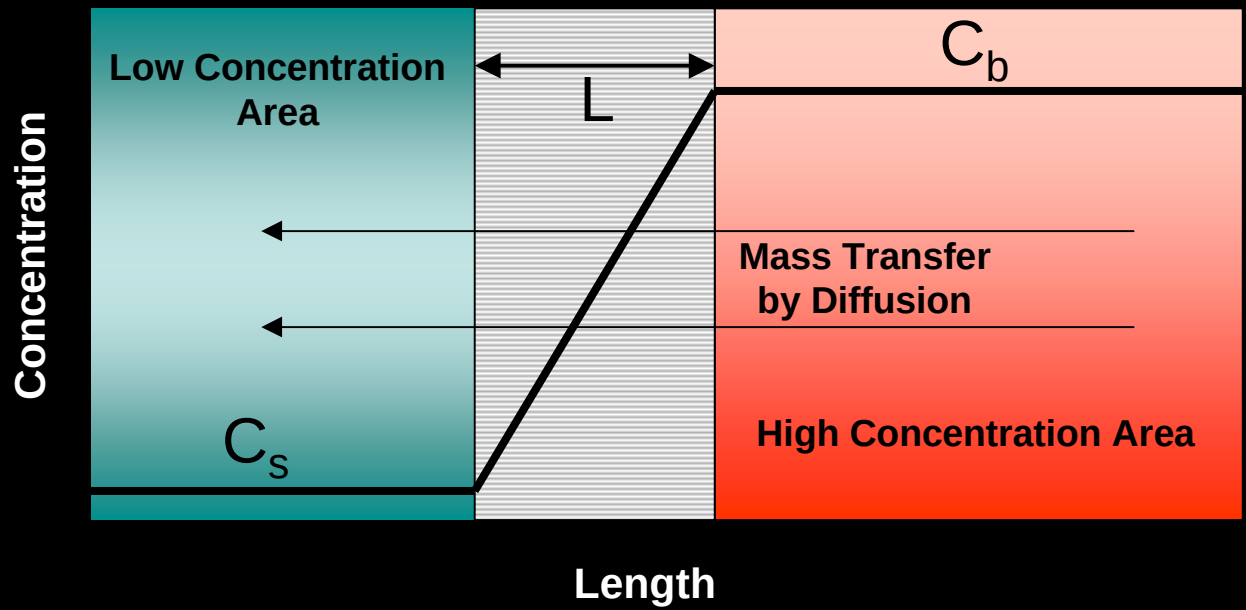
Law of Diffusion



Principle

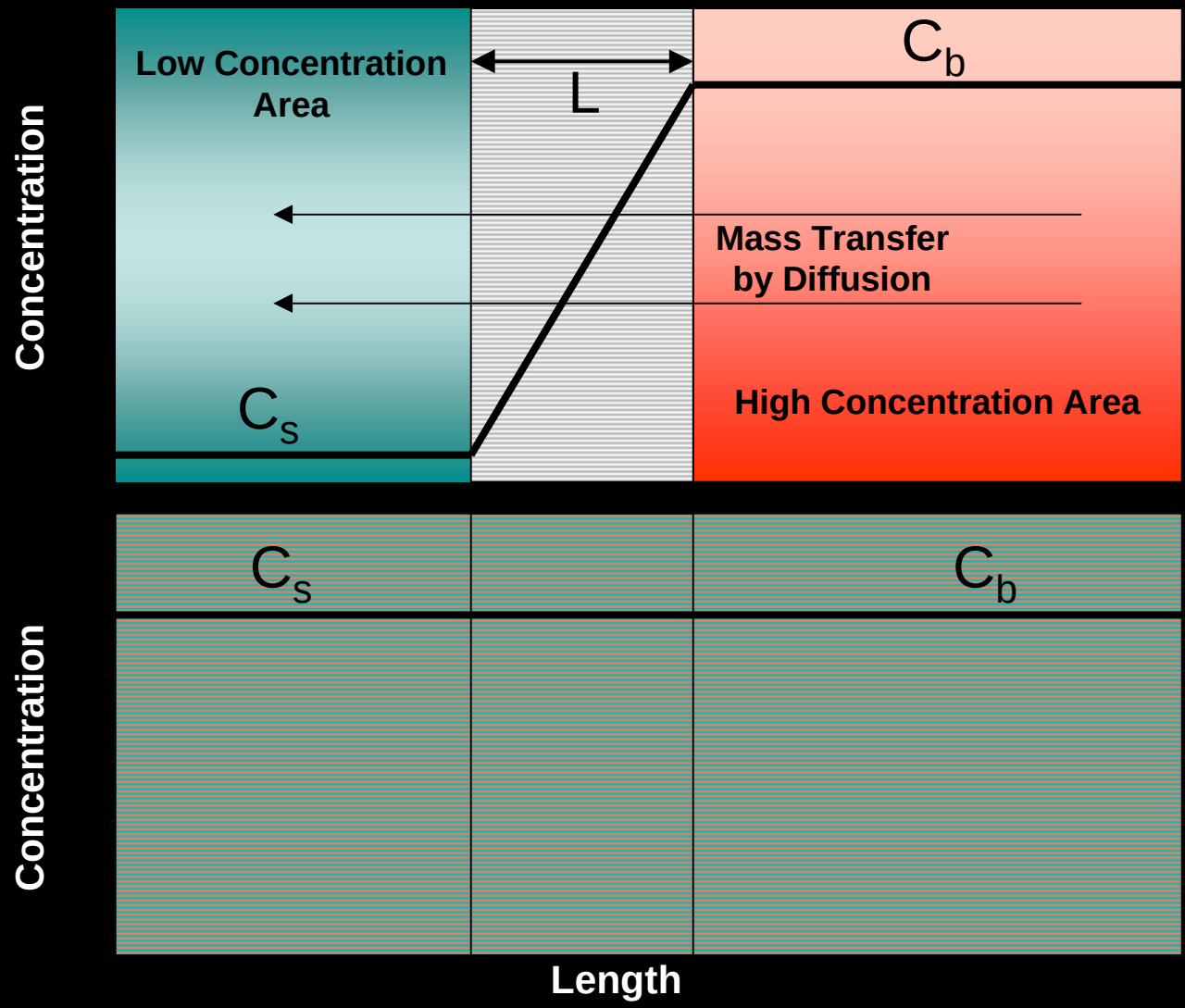
Law of Diffusion (cont.)

Fick's Law: $$J = \frac{D}{L}(C_b - C_s)$$



Principle

Law of Diffusion (cont.)



Two Types of Samplers

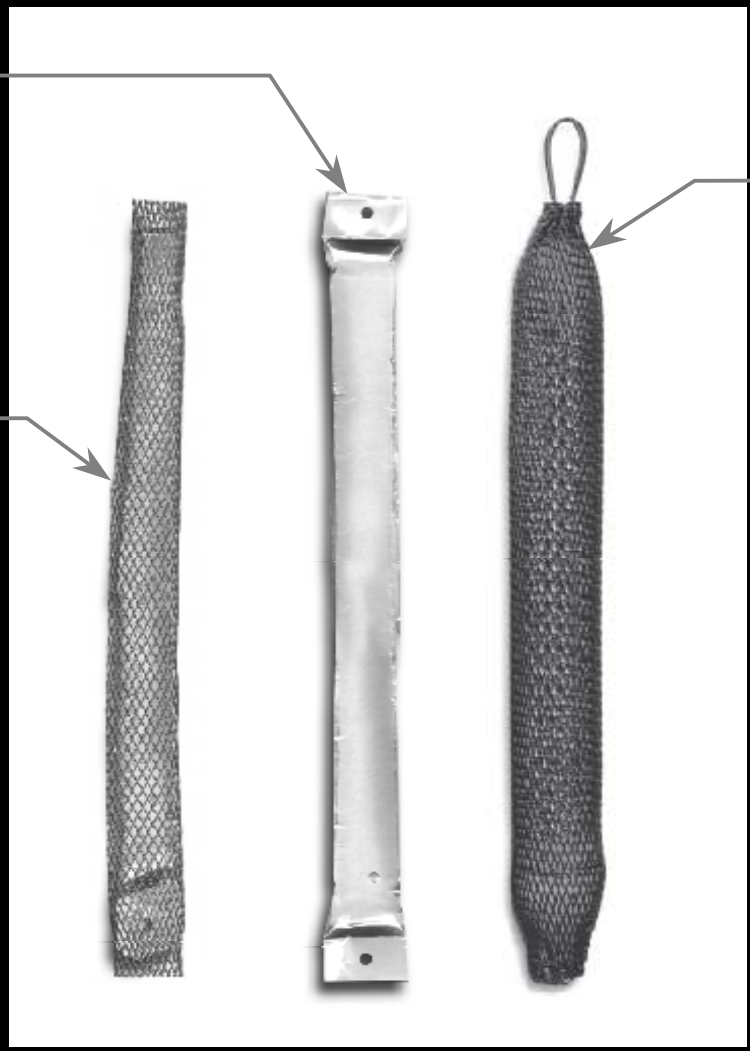
Diffusion Samplers

- PDB
  - Water-filled passive diffusion bag samplers
- PVD
  - Vapor-filled passive vapor diffusion samplers

Typical Water-Filled Diffusion Samplers

PDB sampler without protective mesh

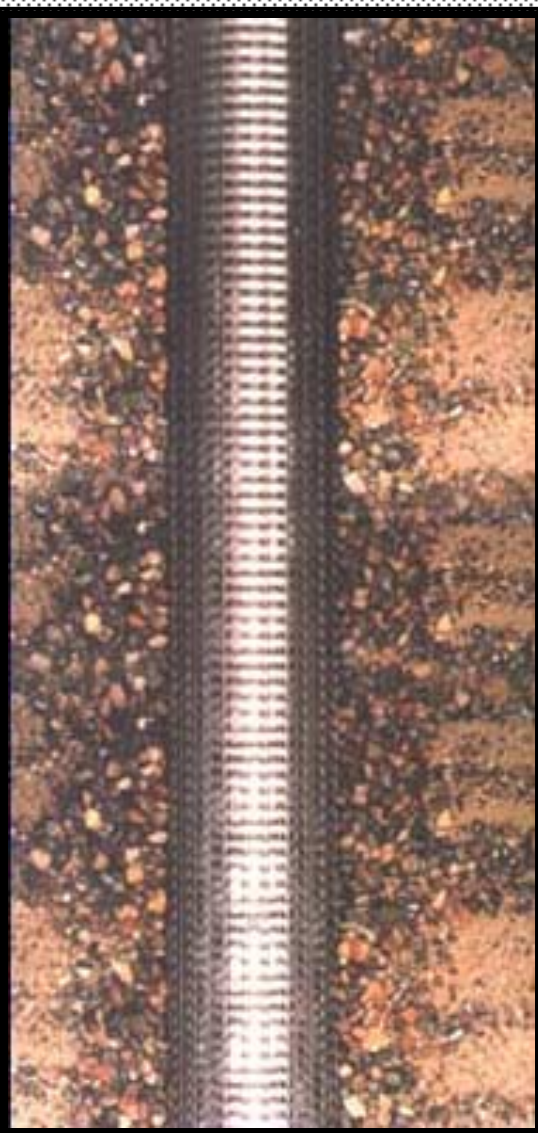
PDB sampler with protective mesh



PDB sampler attached to bailer bottom

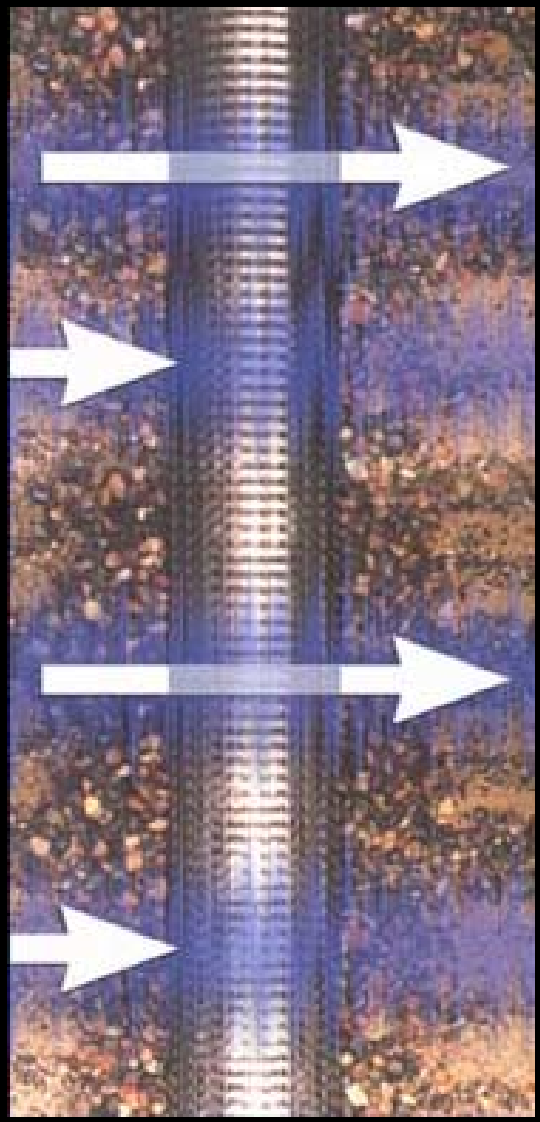
Well Screen

Cross Section View



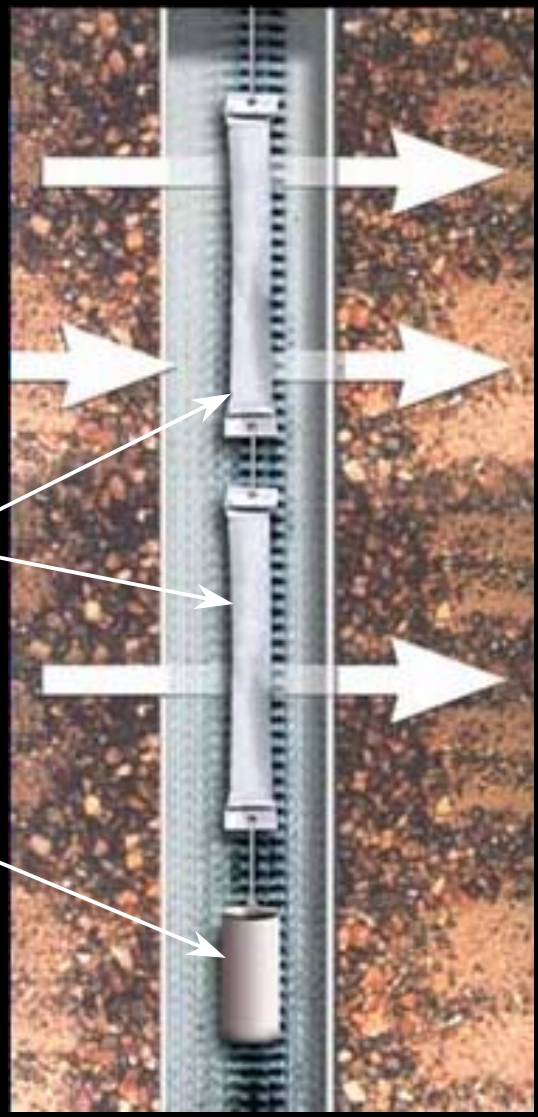
Groundwater and Contaminant Flow

Cross Section View



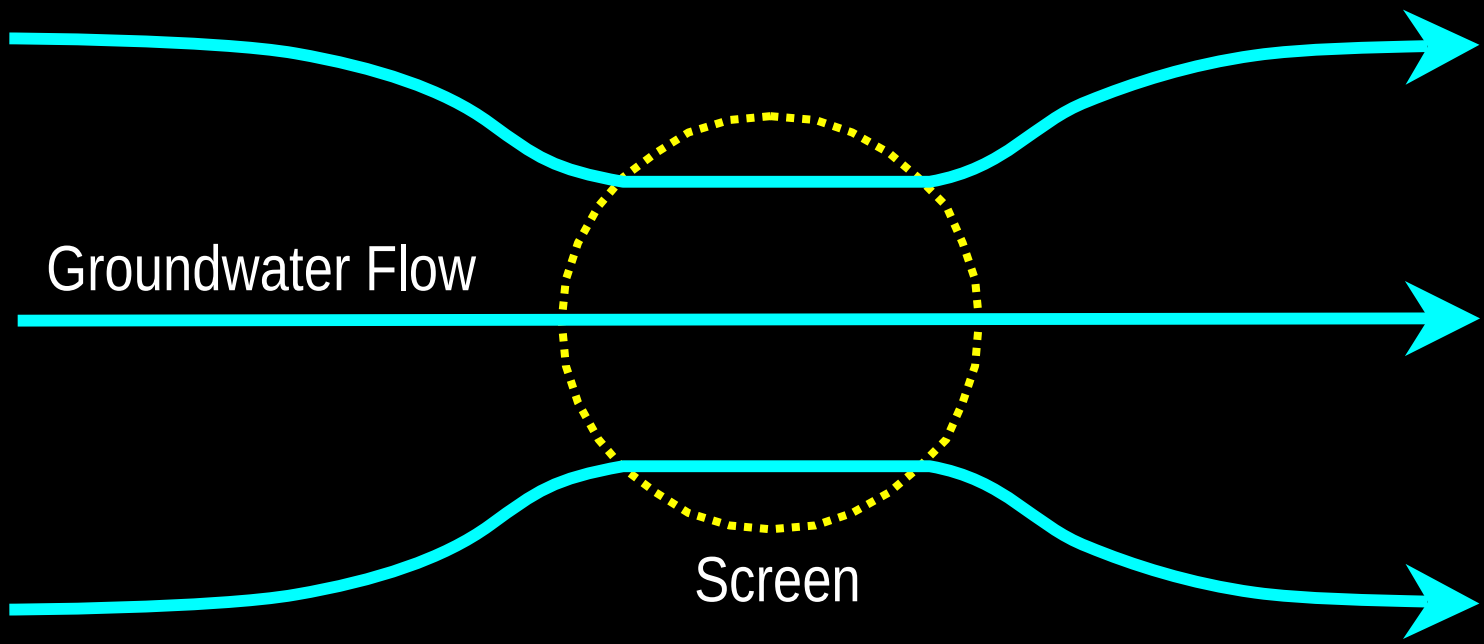
Diffusion Samplers Deployed in Well

Cross Section View



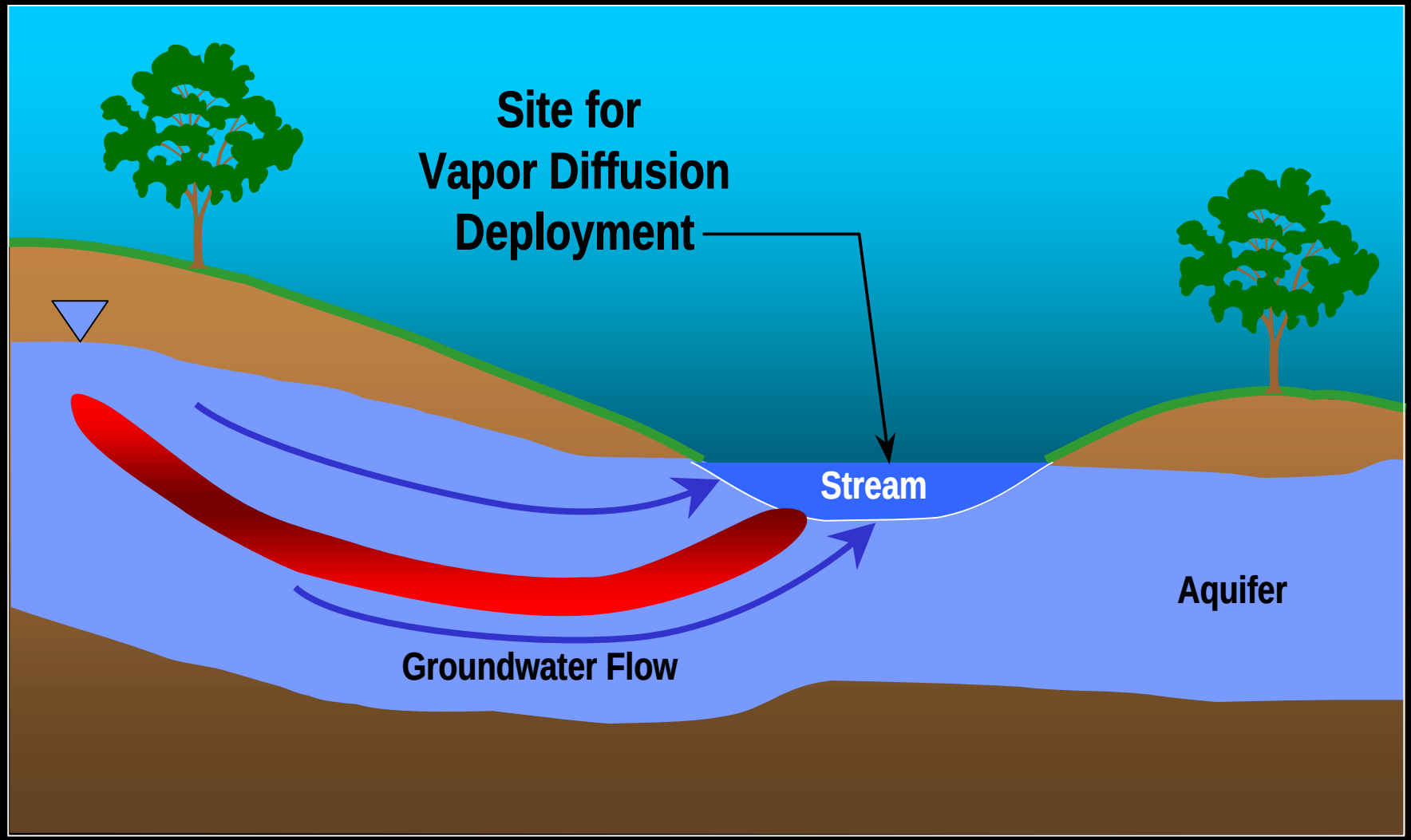
Groundwater Flow Through a Well Screen

Plan View

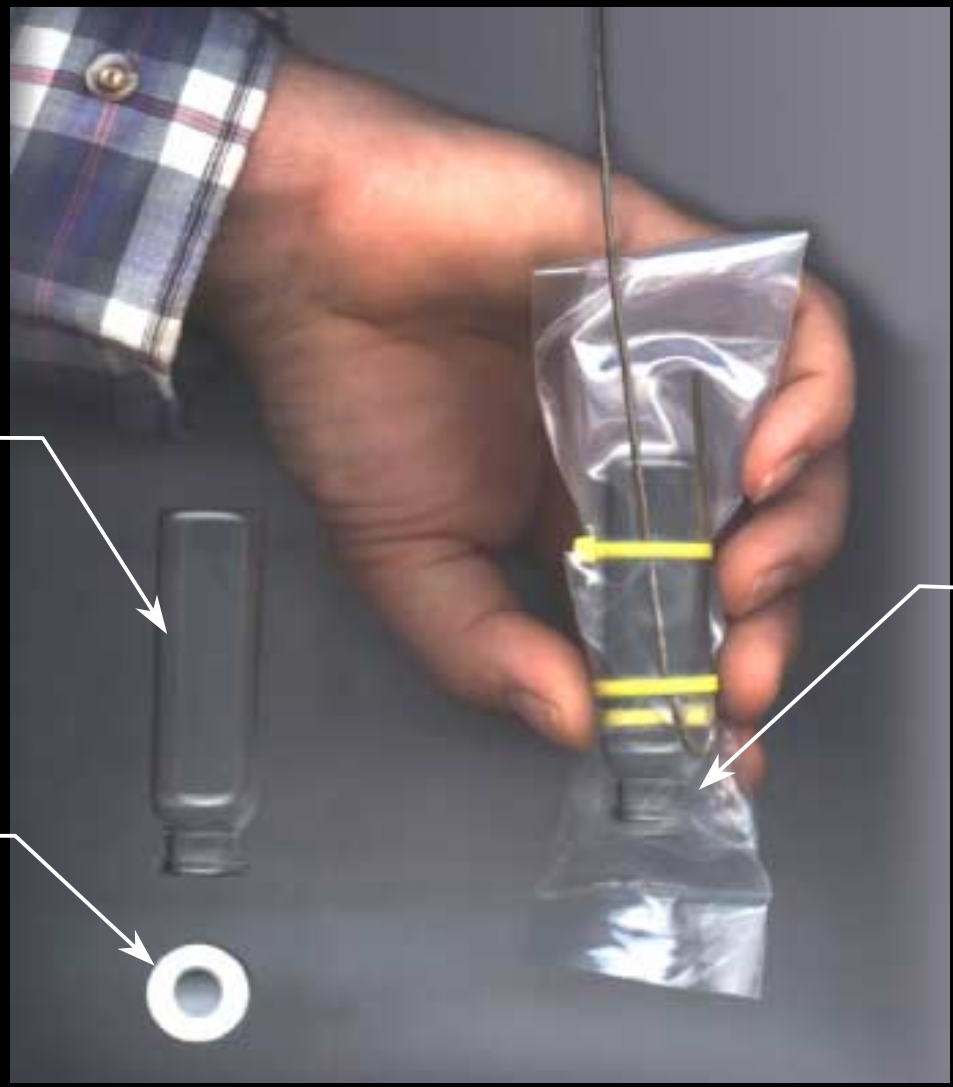


Aquifer Less Permeable Than Well Screen

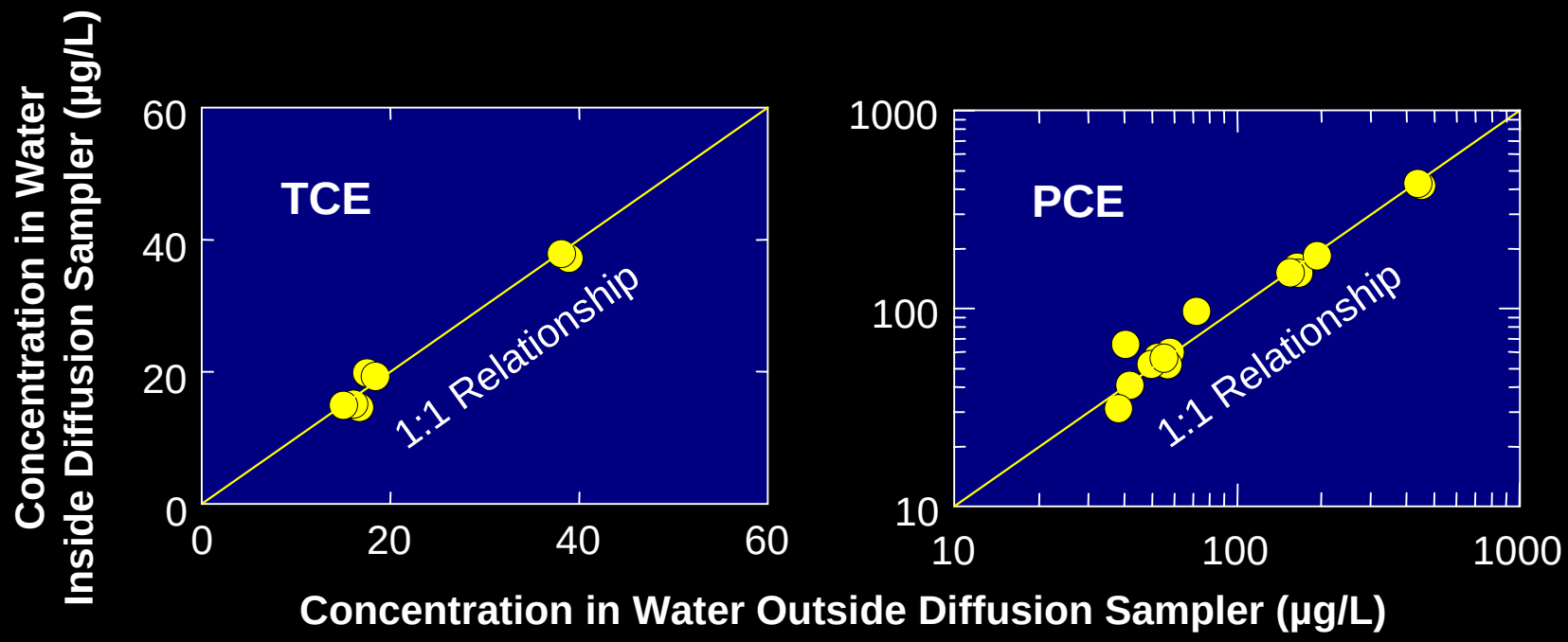
Groundwater Discharge to a Stream



Passive Vapor Diffusion Sampler



Lab Tests of Water-Filled Diffusion (PDB) Samplers



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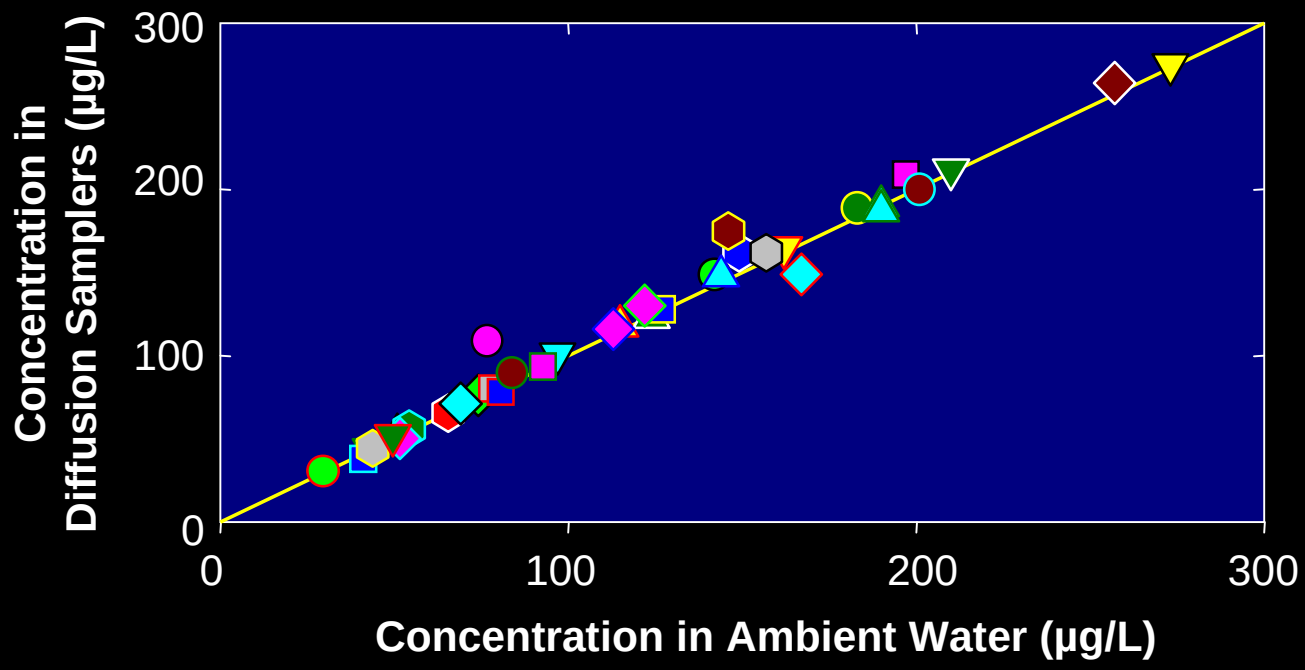
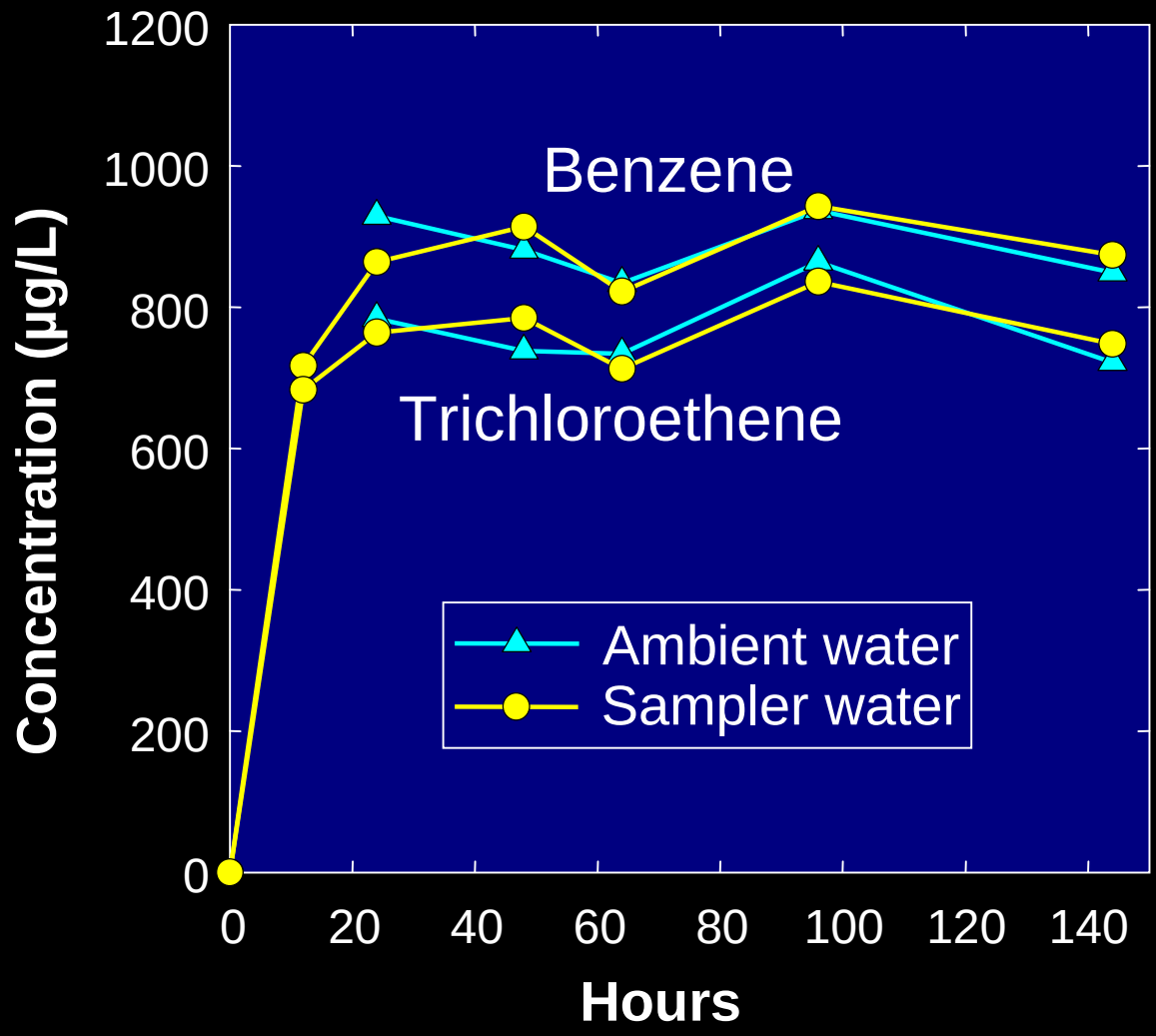


Benzene	EDB	1,2-DCA	Ethyl Benzene	1,1,2-TCA
BDCM	DBM	1,1-DCE	MC	TCE
Bromoform	1,2-DCB	*c*-DCE	Naphthalene	TCFM
Carbon Tet.	1,3-DCB	*t*-DCE	PCA	1,2,3-TCPA
Chlorobenzene	1,4-DCB	1,2-DCPA	PCE	Vinyl Chloride
Chloroethane	DCDFM	*c*-DCPE	Toluene	Total Xylenes
DBCM	1,1-DCA	*t*-DCPE	1,1,1-TCA	

Equilibrium of Water-Filled Diffusion Samplers

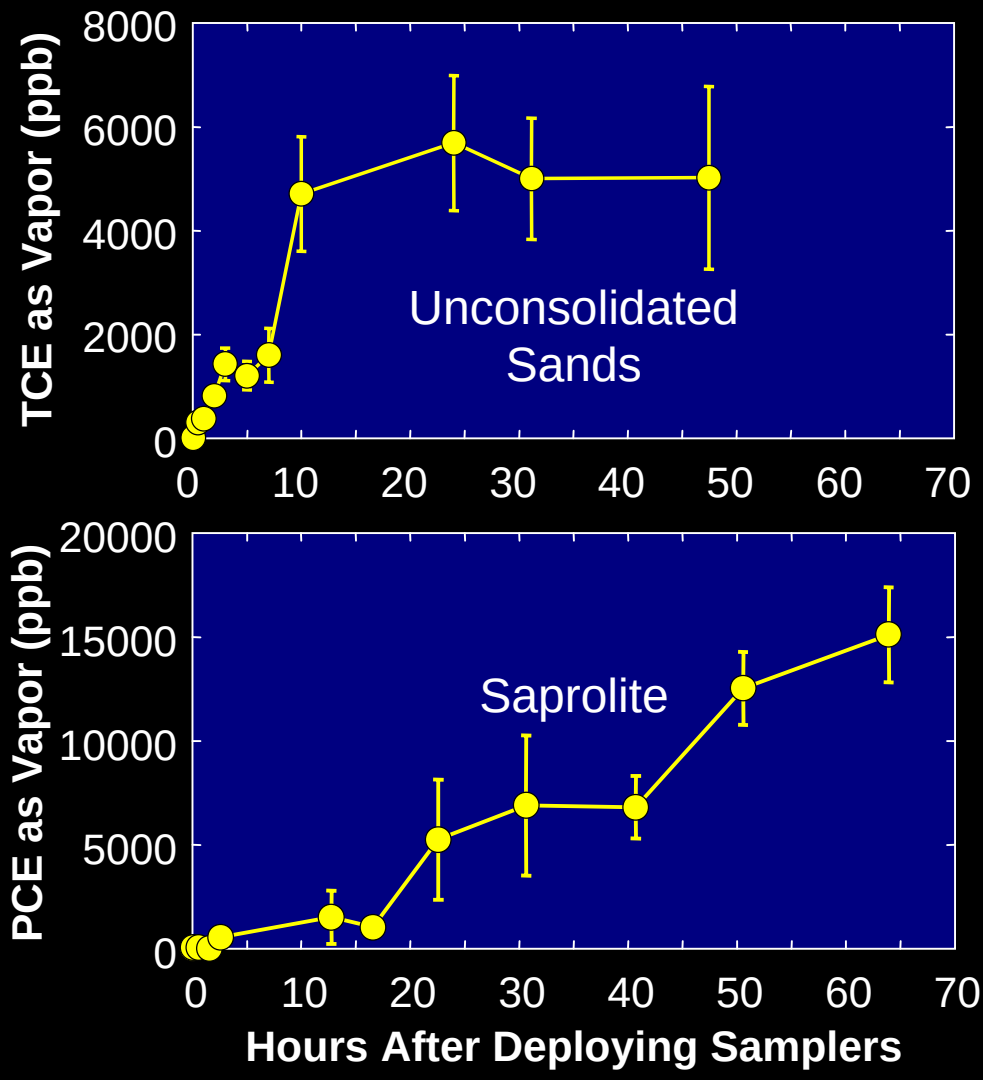
Laboratory Test



PDB Sampler Equilibration in Lab Studies

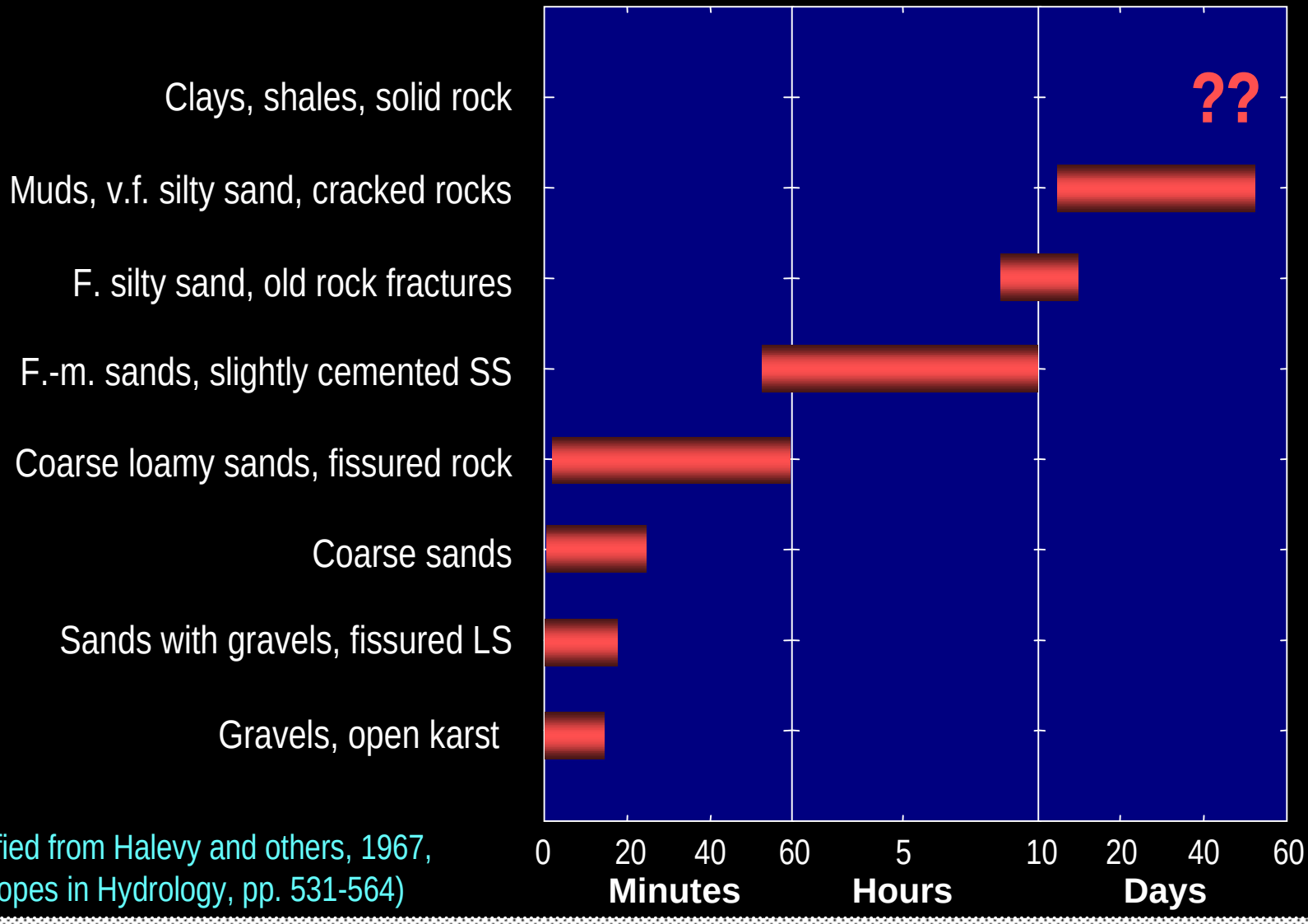
- 48 hours for TCE and several tested compounds (Vroblesky, 2000, USGS)
- 98 to 168 hours for VC and some chloroethenes (Sivavec and Baghel, 2000, General Electric Company)
- But samplers should equilibrate long enough for well water, contaminant distribution, and flow dynamics to restabilize (typically 2 weeks)

Eqilibration Times of WVD Samplers Beneath Streams



Time for a Well to Recover 99% of Predisturbance Concentrations

Diffusion Samplers



(Modified from Halevy and others, 1967, Isotopes in Hydrology, pp. 531-564)

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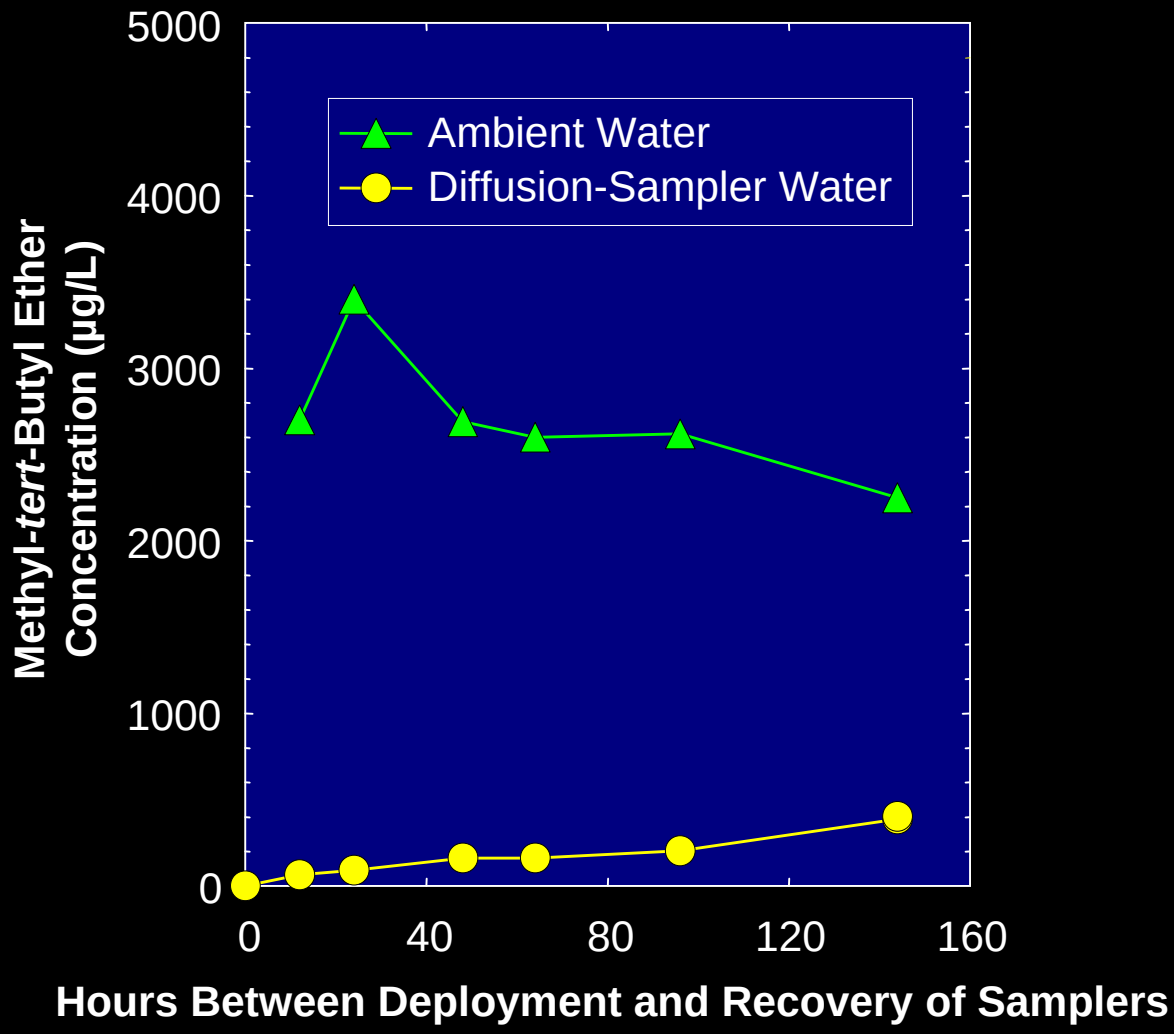
Applicability of Diffusion Samplers

- Applicable to moderately-soluble organic compounds, including the following tested compounds:

Benzene	EDB	1,2-DCA	Ethyl Benzene	1,1,2-TCA
BDCM	DBM	1,1-DCE	MC	TCE
Bromoform	1,2-DCB	*c*-DCE	Naphthalene	TCFM
Carbon Tet.	1,3-DCB	*t*-DCE	PCA	1,2,3-TCPA
Chlorobenzene	1,4-DCB	1,2-DCPA	PCE	Vinyl Chloride
Chloroethane	DCDFM	*c*-DCPE	Toluene	Total Xylenes
DBCM	1,1-DCA	*t*-DCPE	1,1,1-TCA	

MTBE in Diffusion Samplers

Laboratory Test



Applicability of Diffusion Samplers

- Not applicable to inorganic and highly-soluble or highly-insoluble organic compounds, including the following tested compounds:
  - MTBE (too soluble)
  - Pesticides (too insoluble)
  - Most PAHs (naphthalene is an exception)

Applicability of Diffusion Samplers

- At groundwater discharge zones
  - Vapor- and water-filled
- In wells
  - Water-filled

Applicability of Diffusion Samplers

- Low-risk sites in long-term monitoring phase of operations (after response complete)
- Well-characterized sites
- Remote sites where utilities (power and phone) are cost prohibitive
- Caution should be exercised when using diffusion samplers at new or uncharacterized sites

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Costs

Diffusion Samplers

- PDB samplers commercially available at approximately $16.50 to $22.00 each

Costs

Diffusion Samplers

- McClellan AFB Study (McClellan AFB)
  - Cost savings for diffusion sampling estimated at $300 to $800/well
  - Saves about $175,000/yr in IDW disposal
  - Saves about $152,000/yr even without considering IDW costs
- Parsons Engineering Study (McClellan AFB)
  - Estimated cost per sample:
    - $65 for PDB sampling
    - $555 for the DMLS sampling
    - $308 for micropurge sampling
    - $444 for conventional-purge sampling
- USGS Study (Hanscom AFB)
  - Estimated cost per sample:
    - $44 for PDB sampling
    - $72 for low-flow sampling

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Regulatory Issues

Diffusion Samplers

- Samplers are gaining acceptance in regulatory community
- USGS is about to publish a PDB Guidance Document
  - Endorsed by the ITRC, U.S. EPA, AFCEE, and NAVFACENGCOM
  - Anticipated to be available at www.epa.gov (U.S. EPA web address) by December 2000
- Draft PDB (passive diffusion bag) Guidance Document
  - Available at www.nfesc.navy.mil (NFESC web address)
- PVD (passive vapor diffusion) Guidance Document
  - Being written by USGS
  - Expected publication date early 2001

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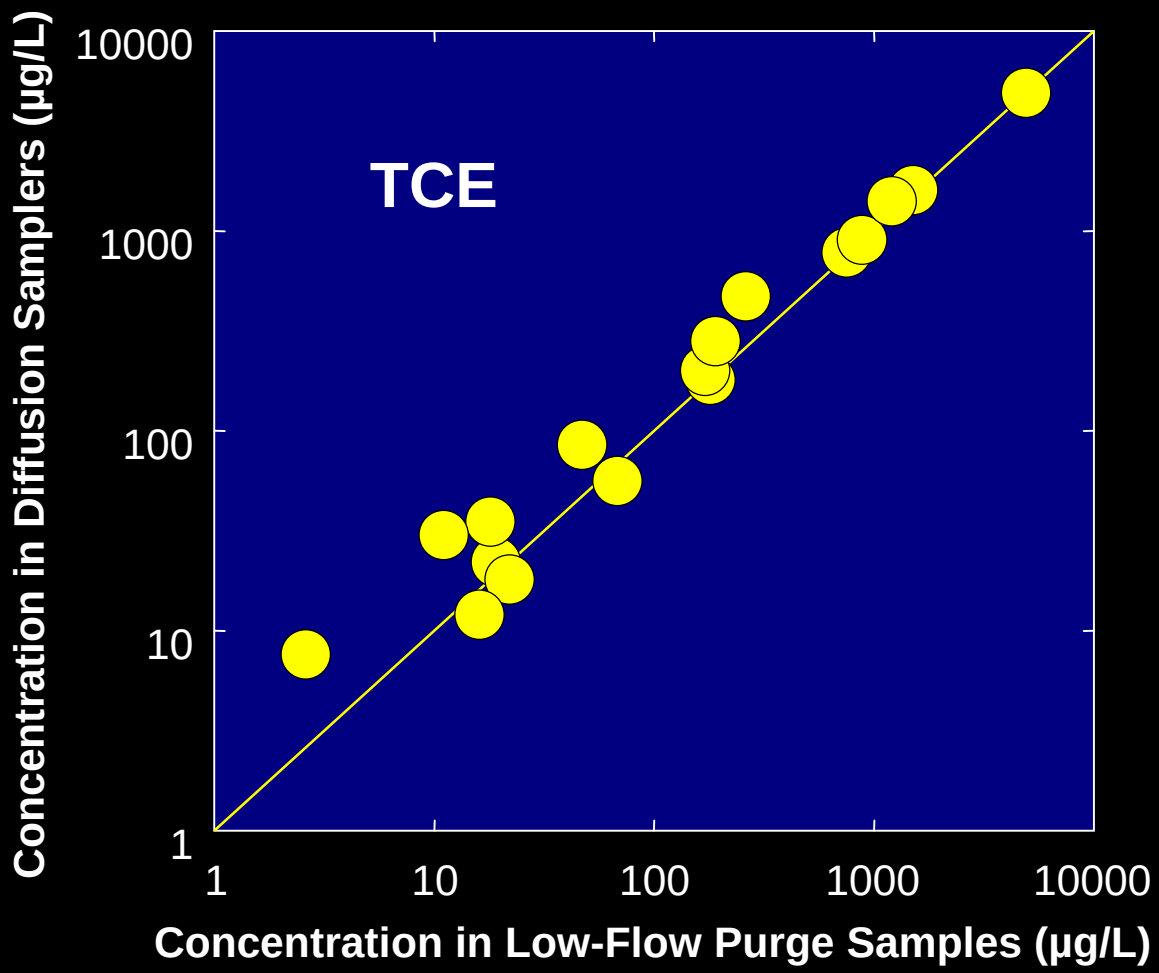
Diffusion Samplers

Hanscom AFB (May 1999): Fractured Rock and Overburden



(Data from Peter Church, USGS)

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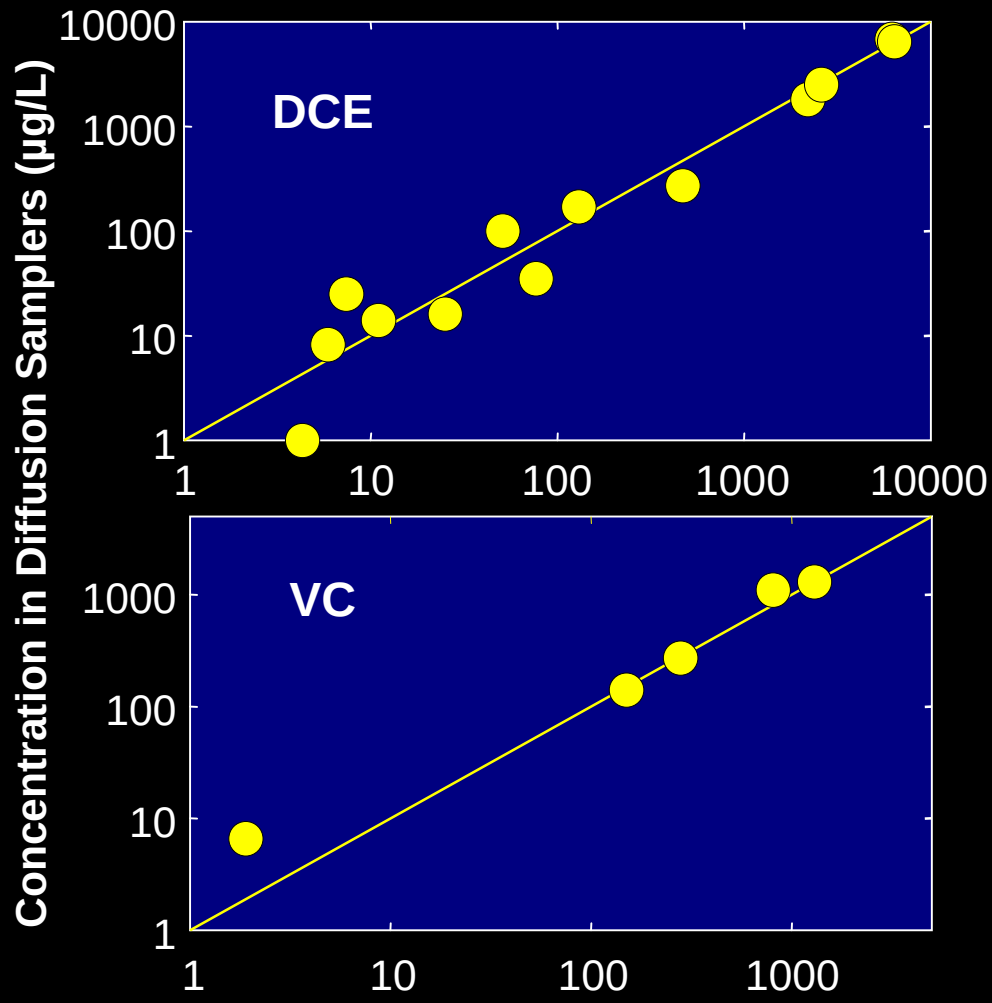
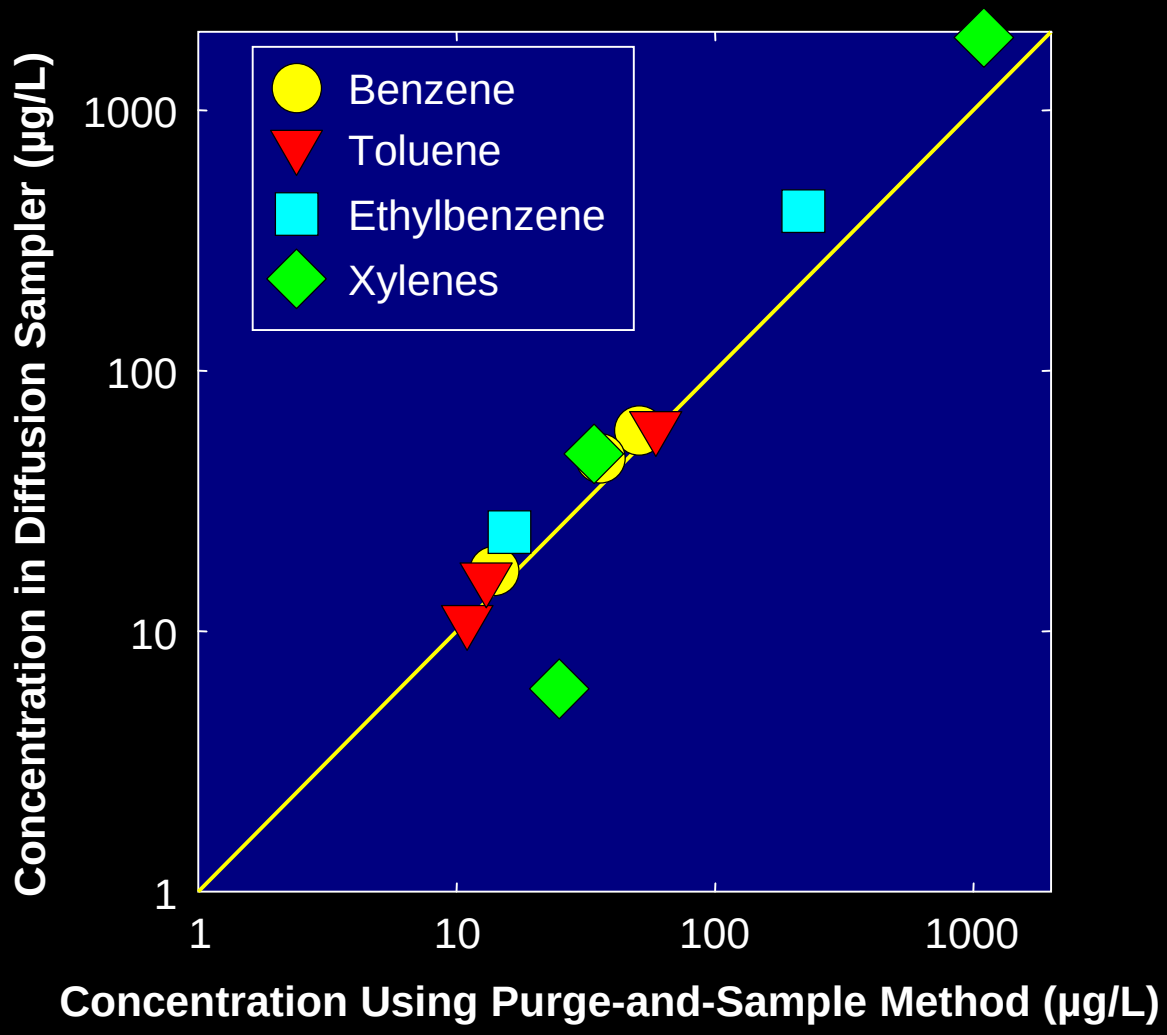


(Data from Peter Church, USGS)

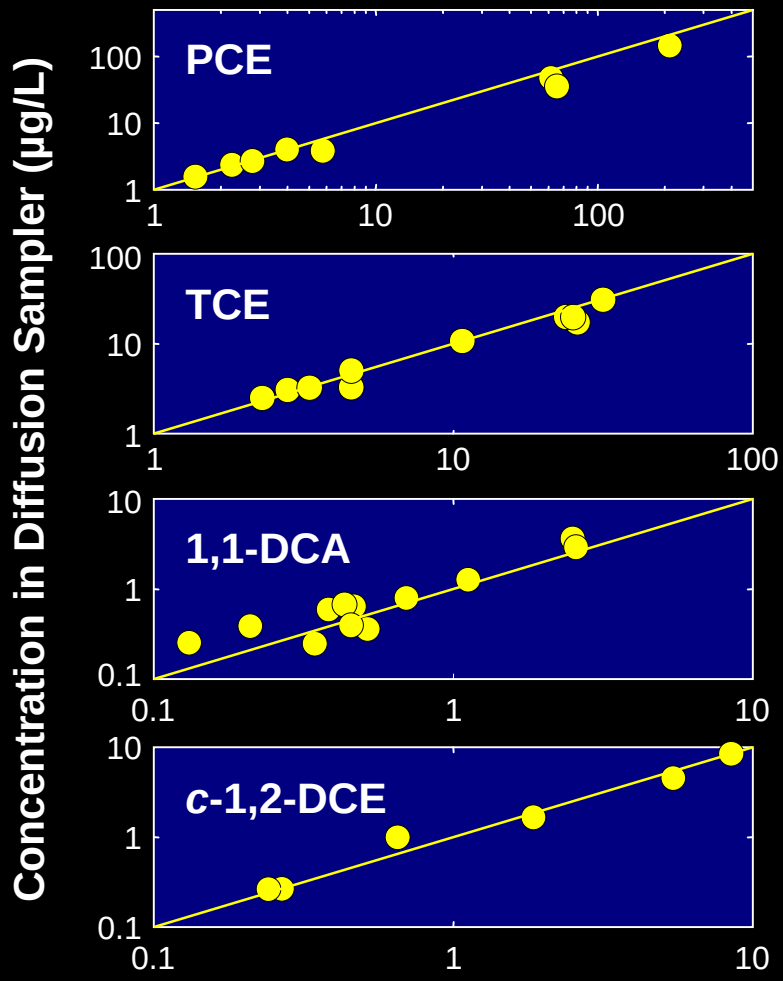
BTEX Data From Fractured-Rock Aquifer

NSWC, Louisville, KY



Diffusion vs. Purge-and-Sample

Davis, CA (Jan. 1999)

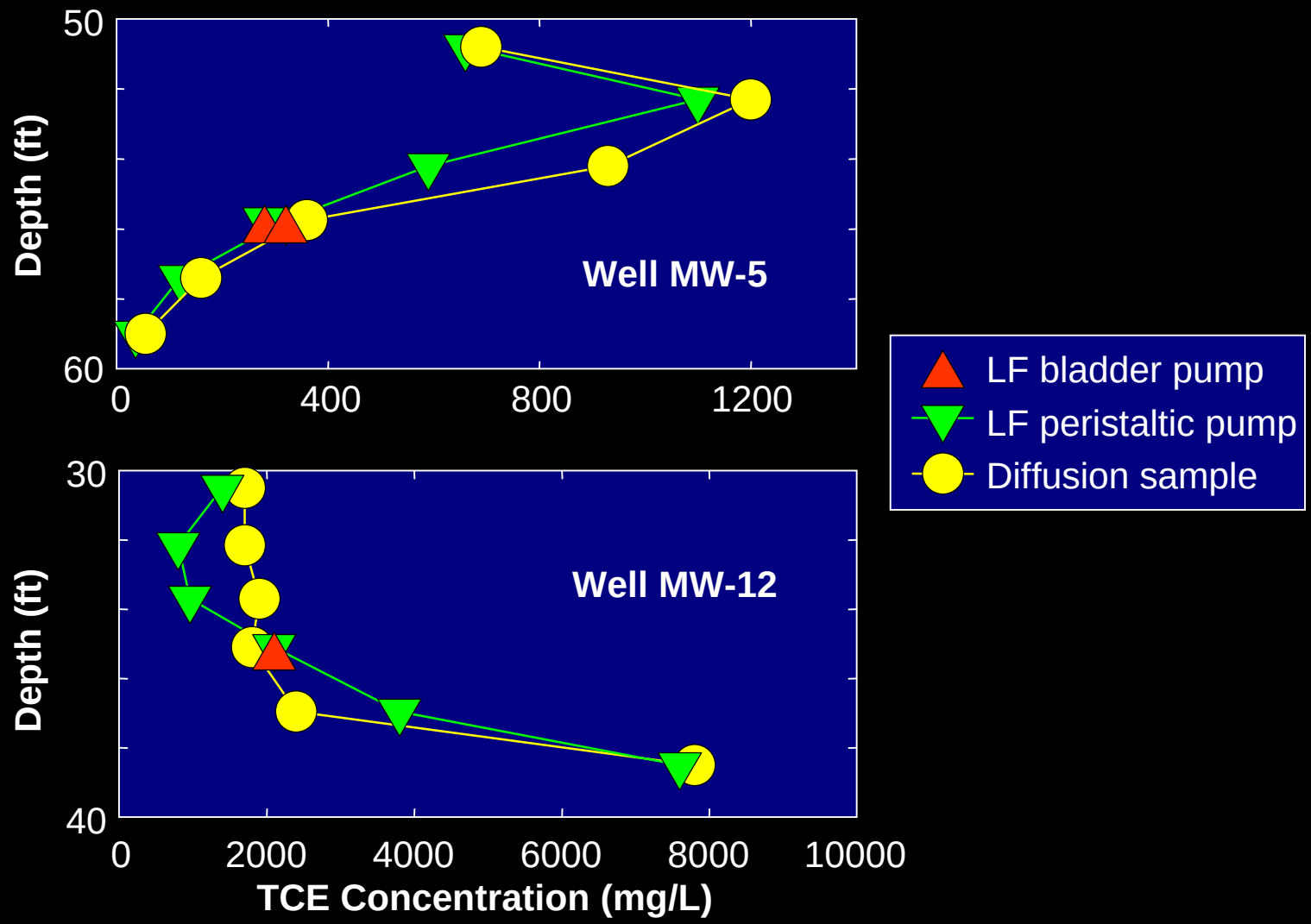


Multiple Diffusion Samplers

Used to Investigate Contaminant Stratification

TCE Stratification in 10-Ft Well Screens

NAS North Island, CA



Comparison of PDB and Purge Sampling Methods

Fridley, MN (Nov. 1999)

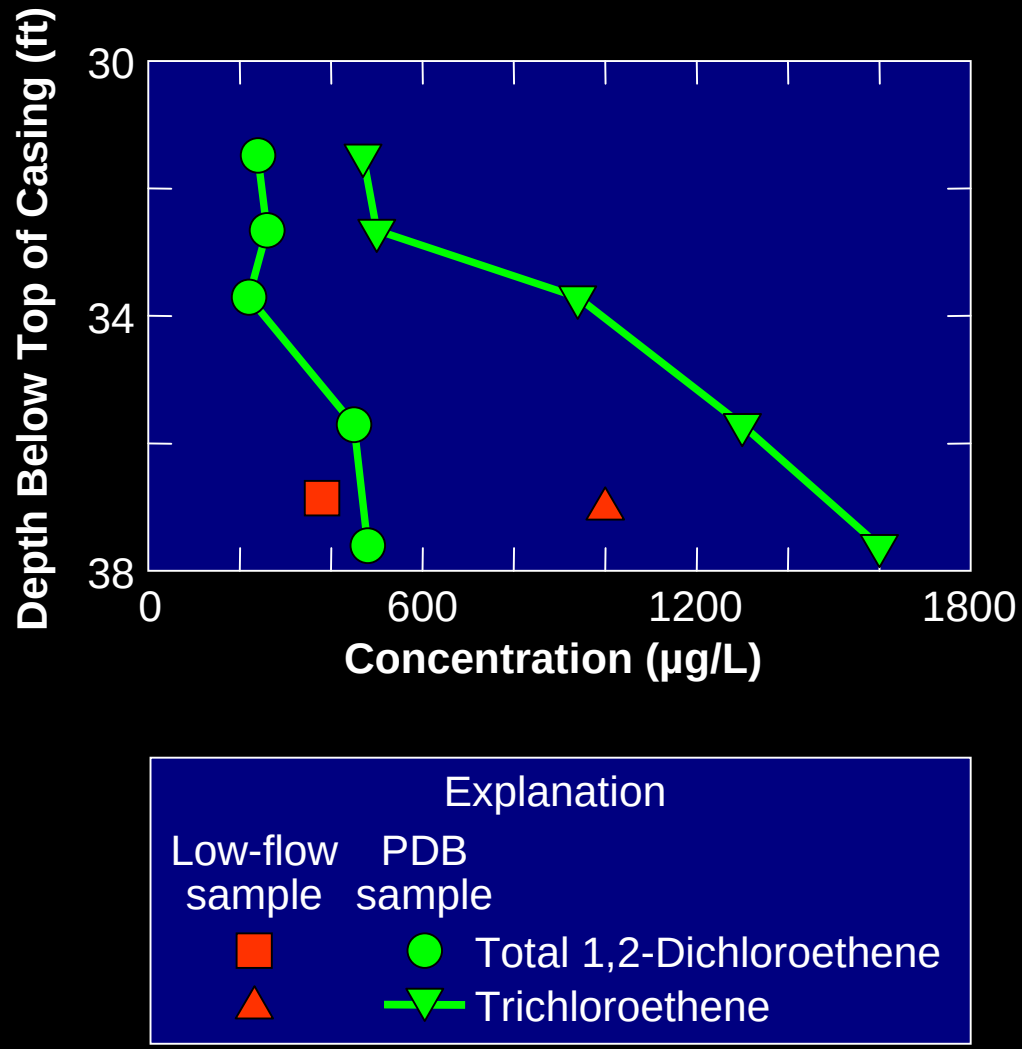
Comparison of PDB and 4-casing-volume purge sampling results, well 18-S

	PDB Sampler Method (µg/L)	Purge-and-Sample Method (µg/L)
Total 1,2-DCE	130	650
TCE	570	2,300

Low-Flow Sampling

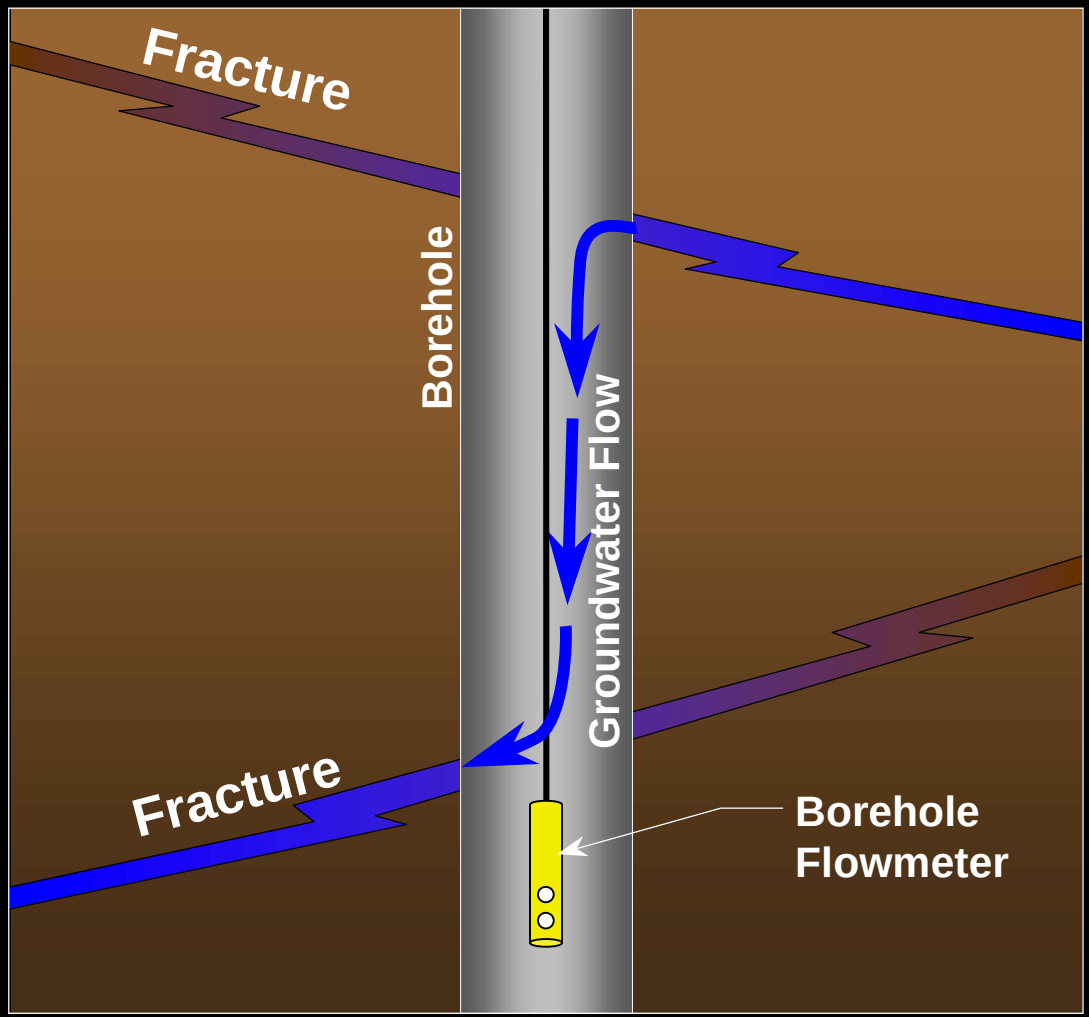
Fridley, MN (May 2000)

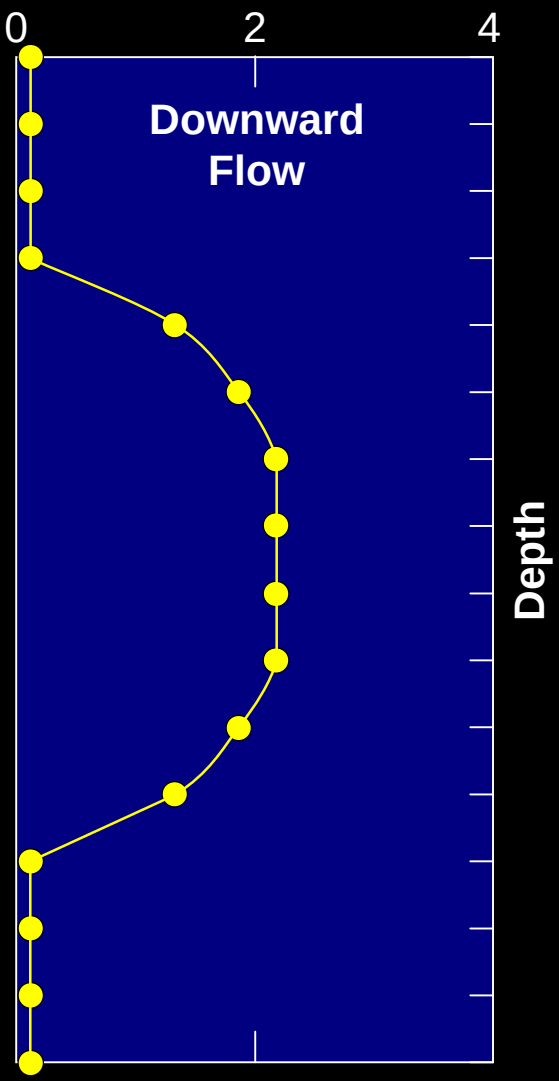
- Retesting of well 18-S by LF and PDB implied that pumping can mix the sample across the screened interval
- Previous 4-casing-volume purge may have pumped higher concentrations from below the screen



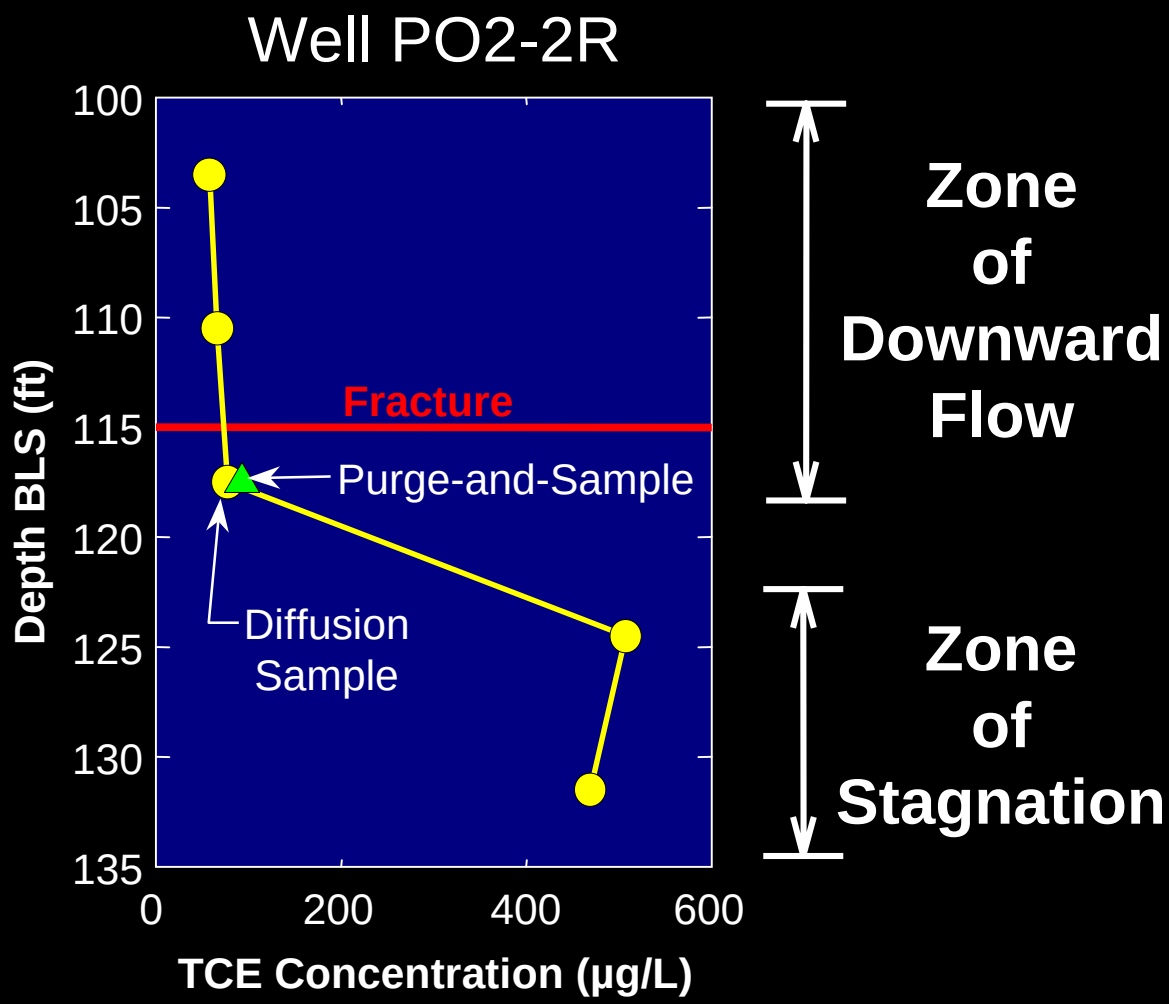
Heat-Pulse Flowmeter

Investigating Vertical Flow in Wells Using Borehole Flowmeter



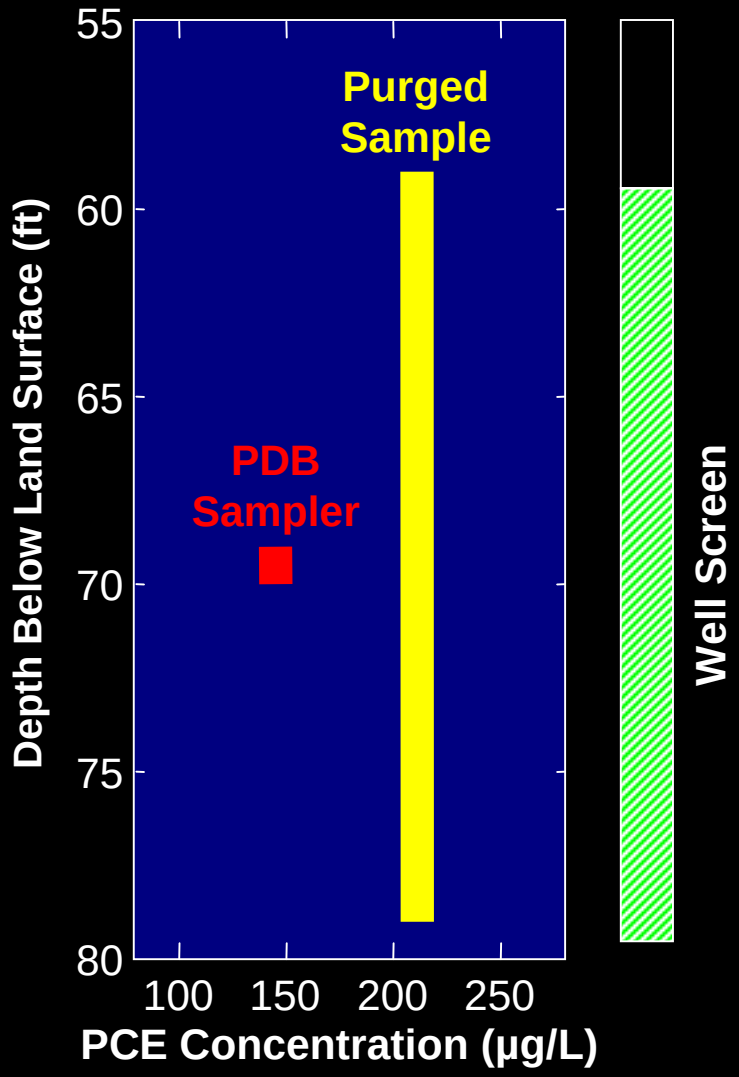


High TCE Concentrations in the Zone of Stagnation



Example of Discrepancy Between Methods

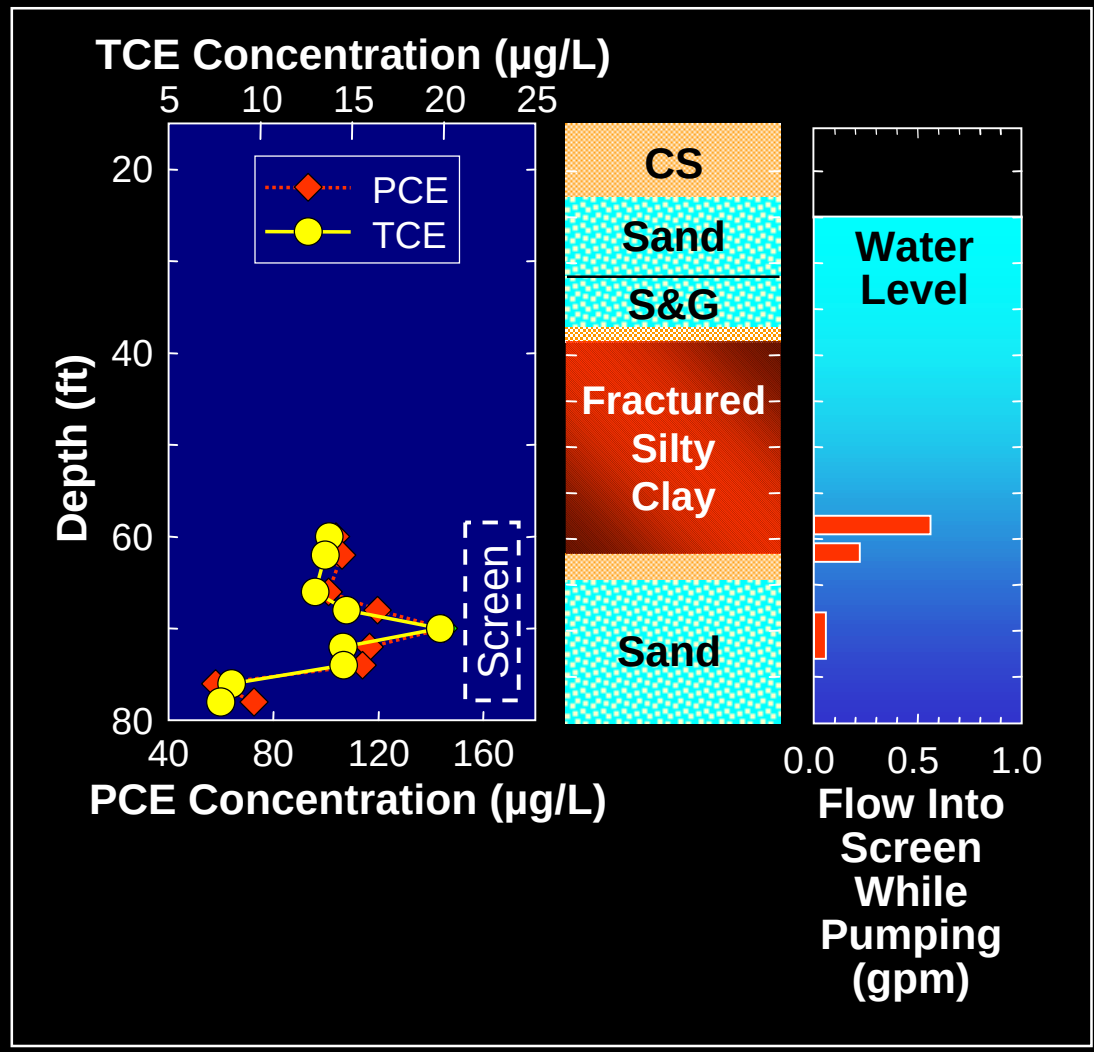
Davis Global Communications, CA: Well DMW-5



Comparison of PDB Sampling and Purge & Sample

Davis Global Communications, CA,: Well DMW-5

- Diffusion method and purge method sampled water from different sources



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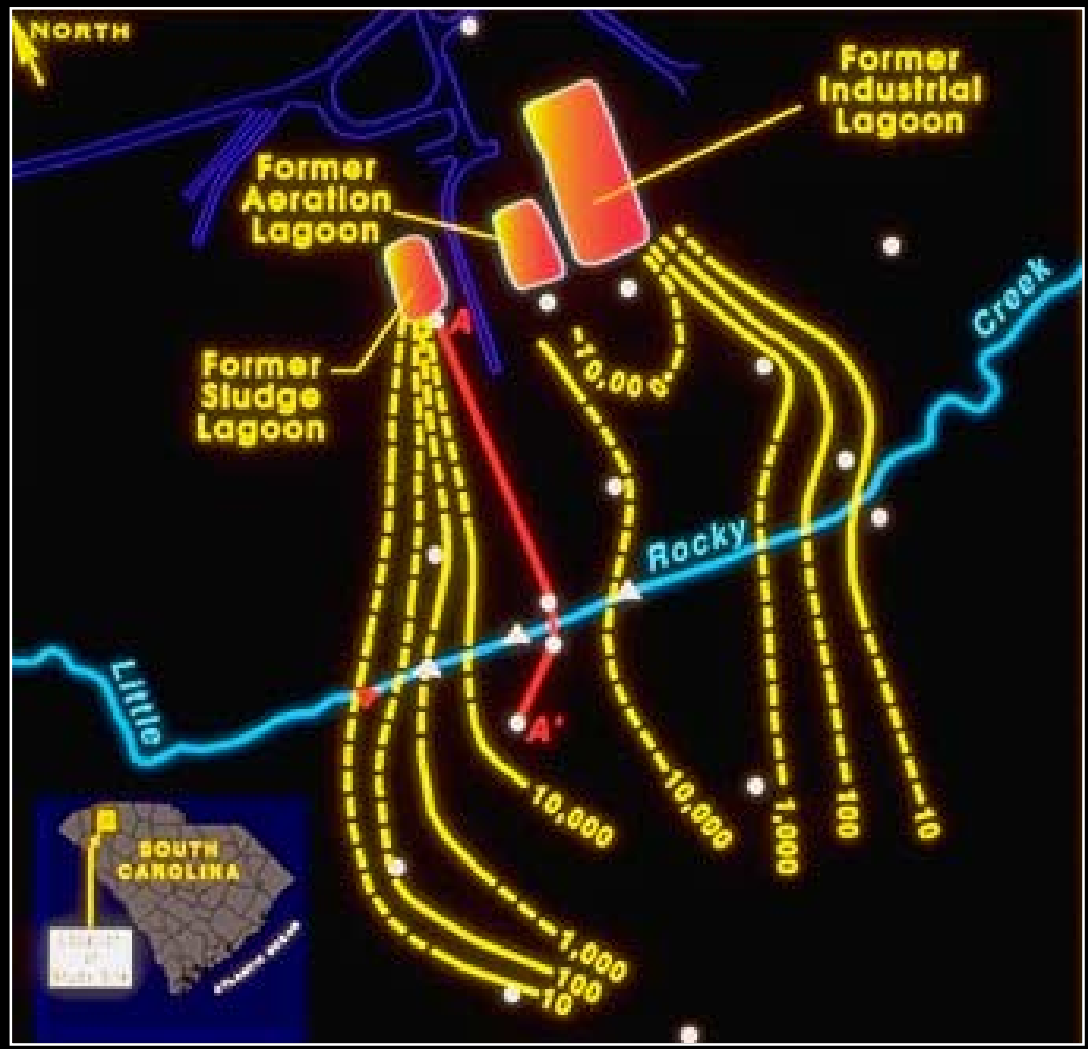
Distribution of VOCs in Fractured-Rock Aquifer

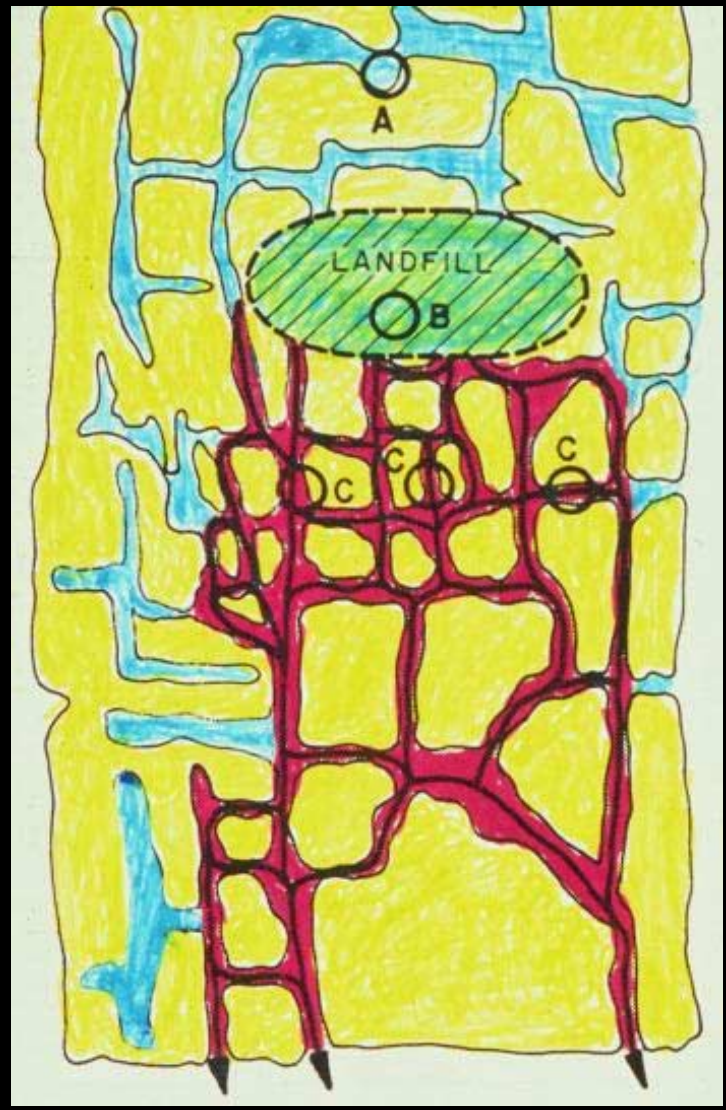
Greenville, SC



Contamination in Fractured-Rock Aquifer

Greenville, SC

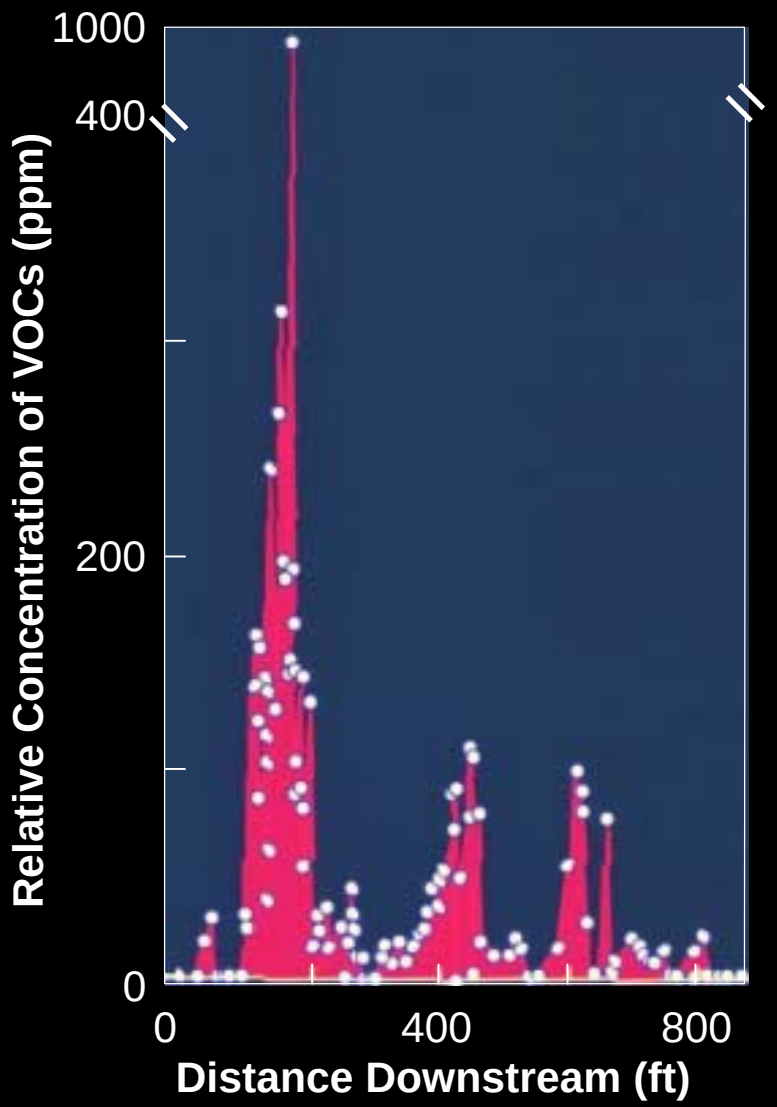
- Idealized Flow Patterns



Groundwater Flow Direction

VOCs in Little Rocky Creek

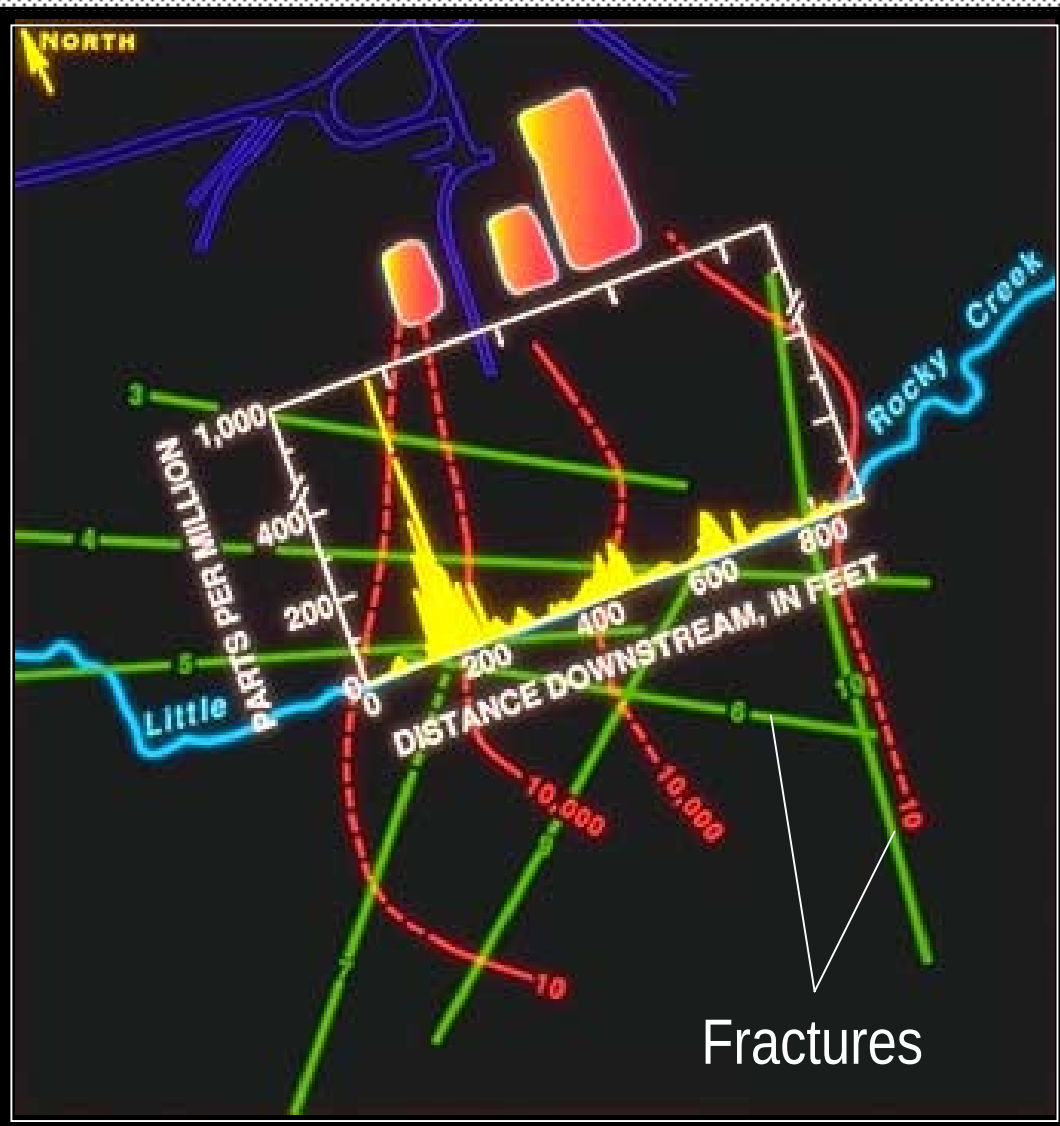
Greenville, SC



VOCs in Little Rocky Creek

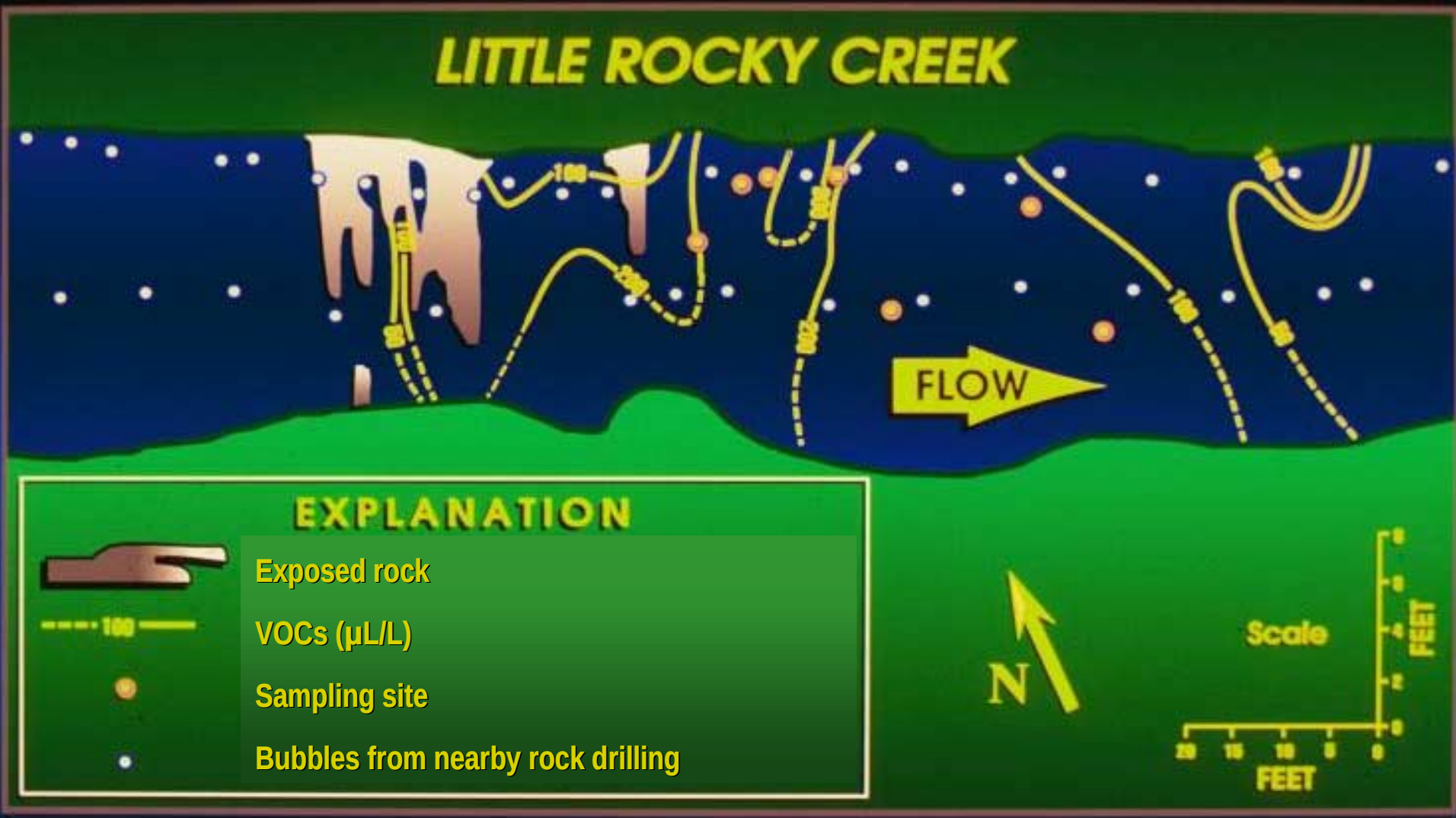
Greenville, SC

- Diffusion samplers show primary VOC discharge zones are at intersection of creek and fractures



Diffusion Samplers in Little Rocky Creek

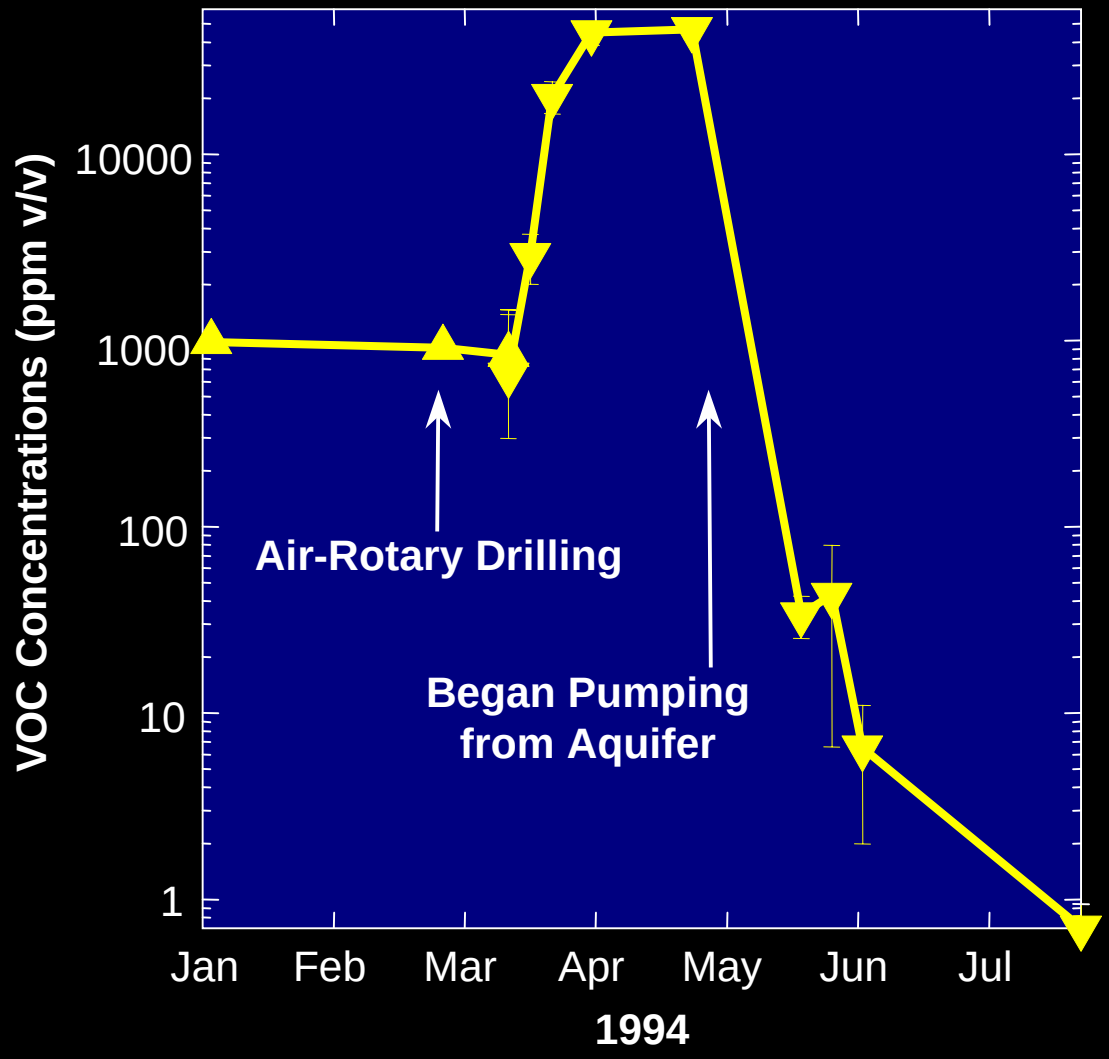
Greenville, SC



Diffusion Samplers in Little Rocky Creek

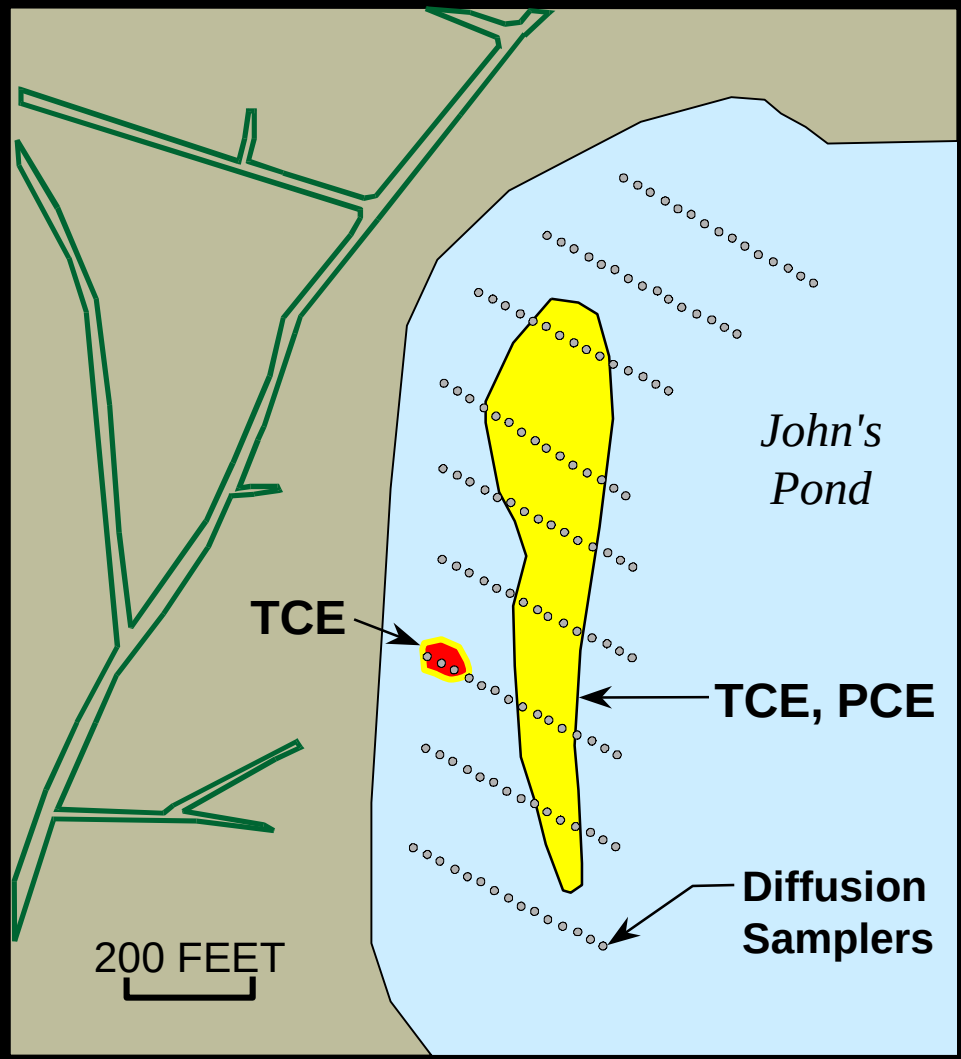
Greenville, SC

- Changes in VOC Concentrations in Vapor-Diffusion Samplers Beneath Little Rocky Creek, SC



Diffusion Samplers in John's Pond

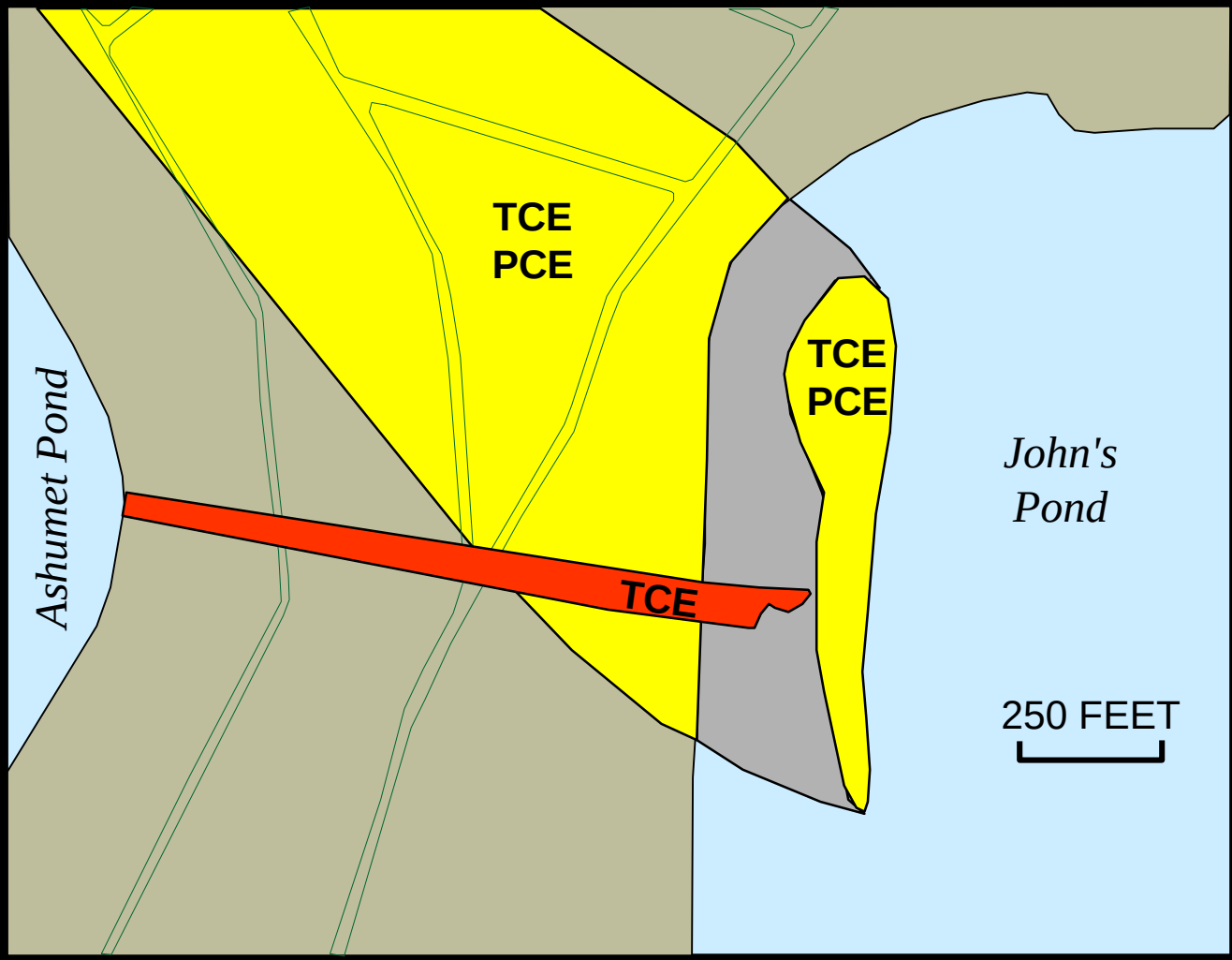
Cape Cod, MA



(Savoi et al, 2000, USGS WRI 4017)

John's Pond and Ashumet Pond

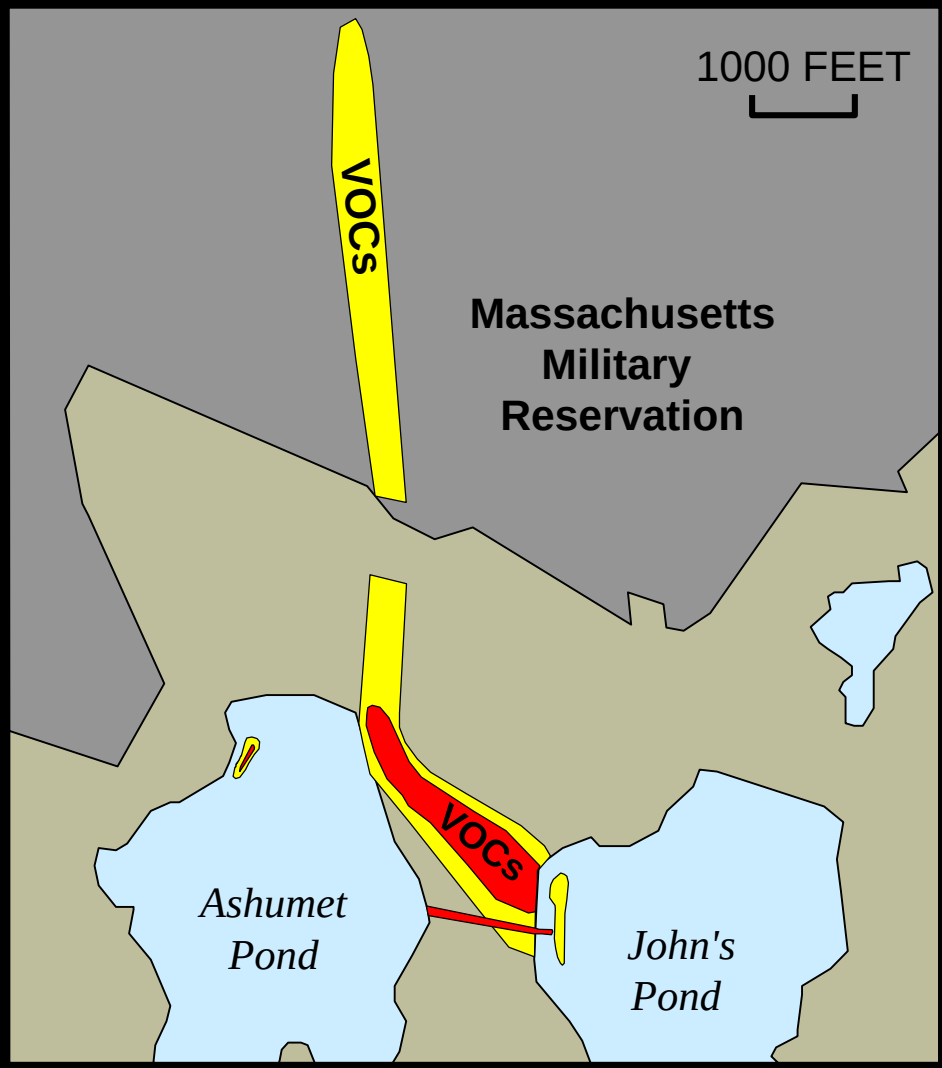
Cape Cod, MA



(Savoi et al, 2000, USGS WRI 4017)

Source of Contamination in Ponds

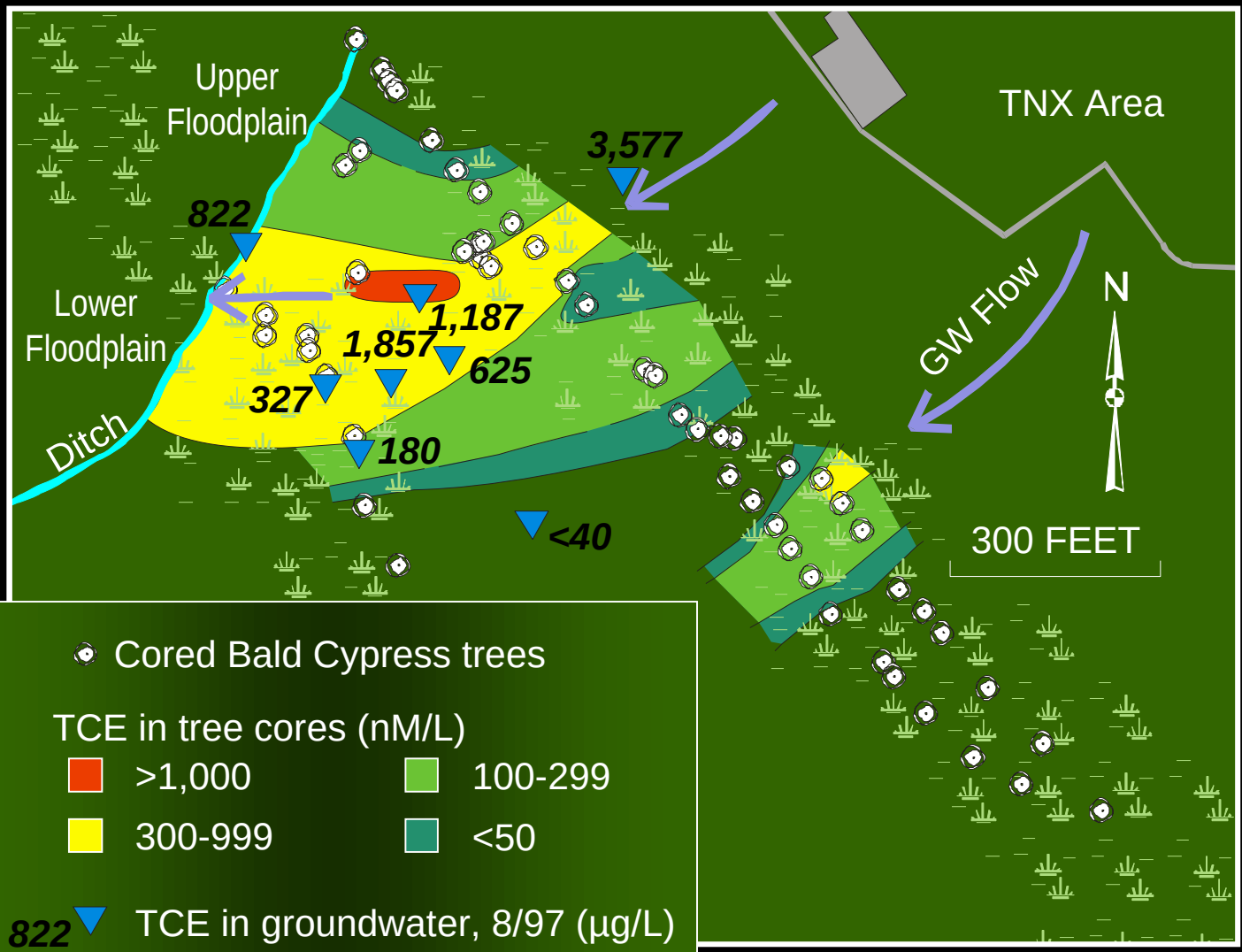
Cape Cod, MA



(Savoi et al, 2000, USGS WRI 4017)

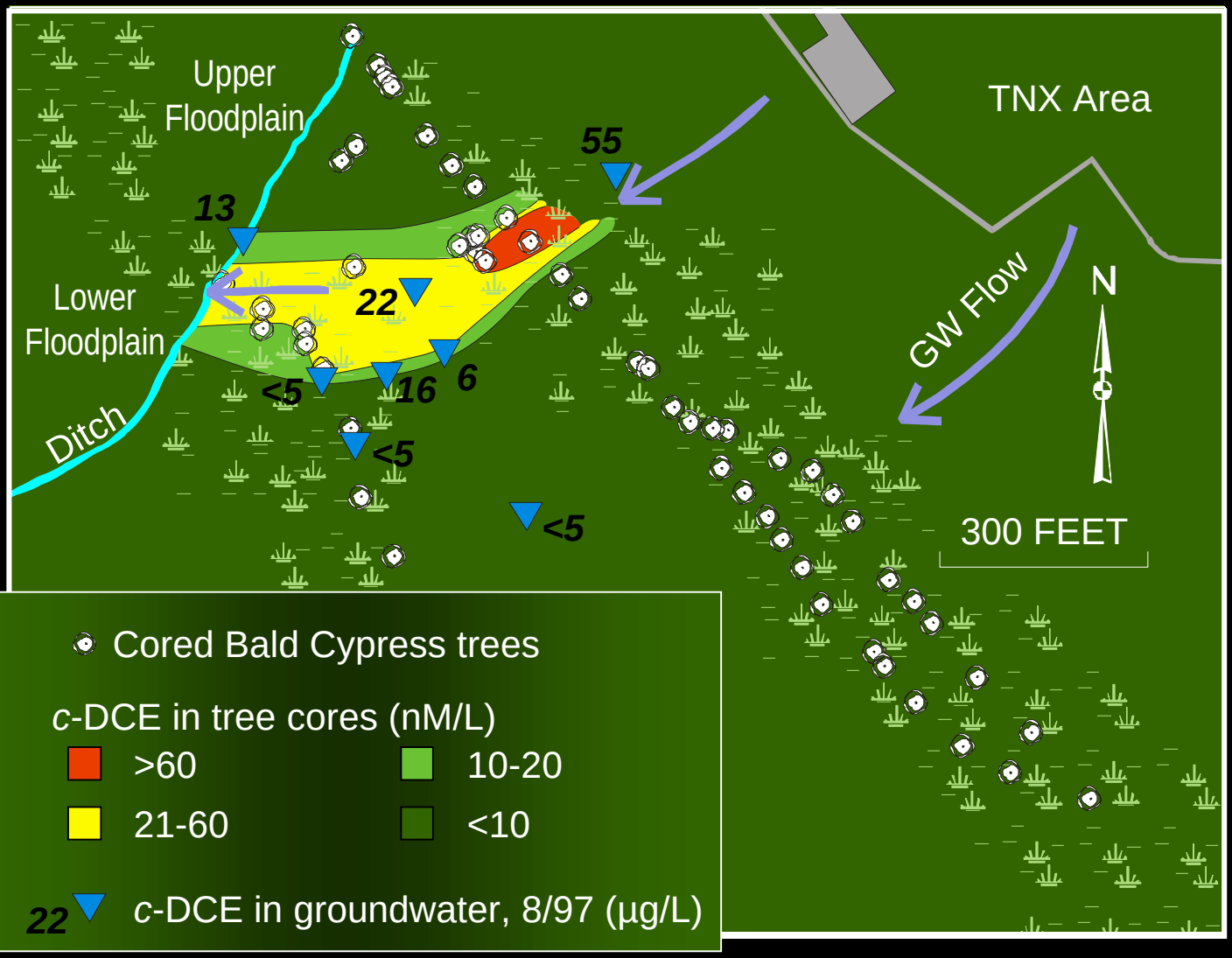
TCE in Bald Cypress Tree Cores

Savannah River Site, SC (Jan-Feb 1998)



c-DCE in Bald Cypress Tree Cores

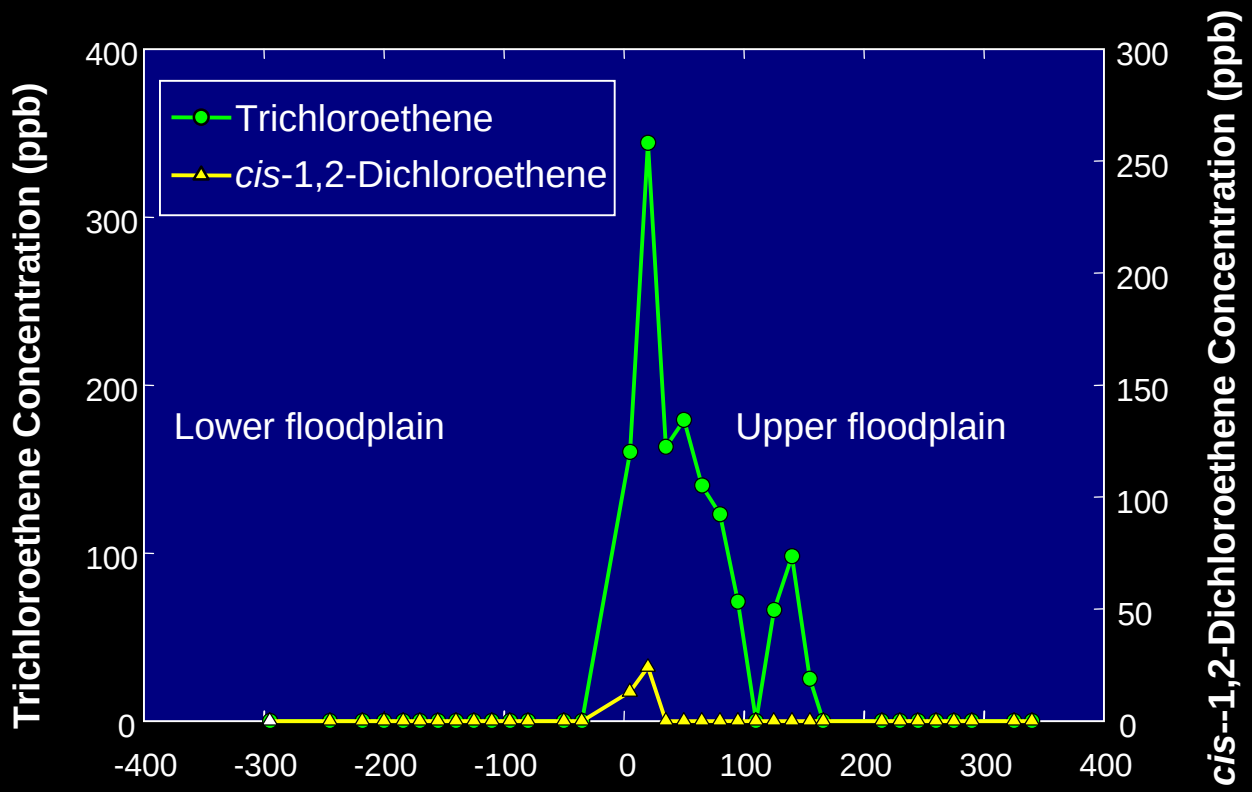
Savannah River Site, SC (Jan-Feb 1998)



TCE and *c*-DCE Concentrations

Savannah River Site, SC

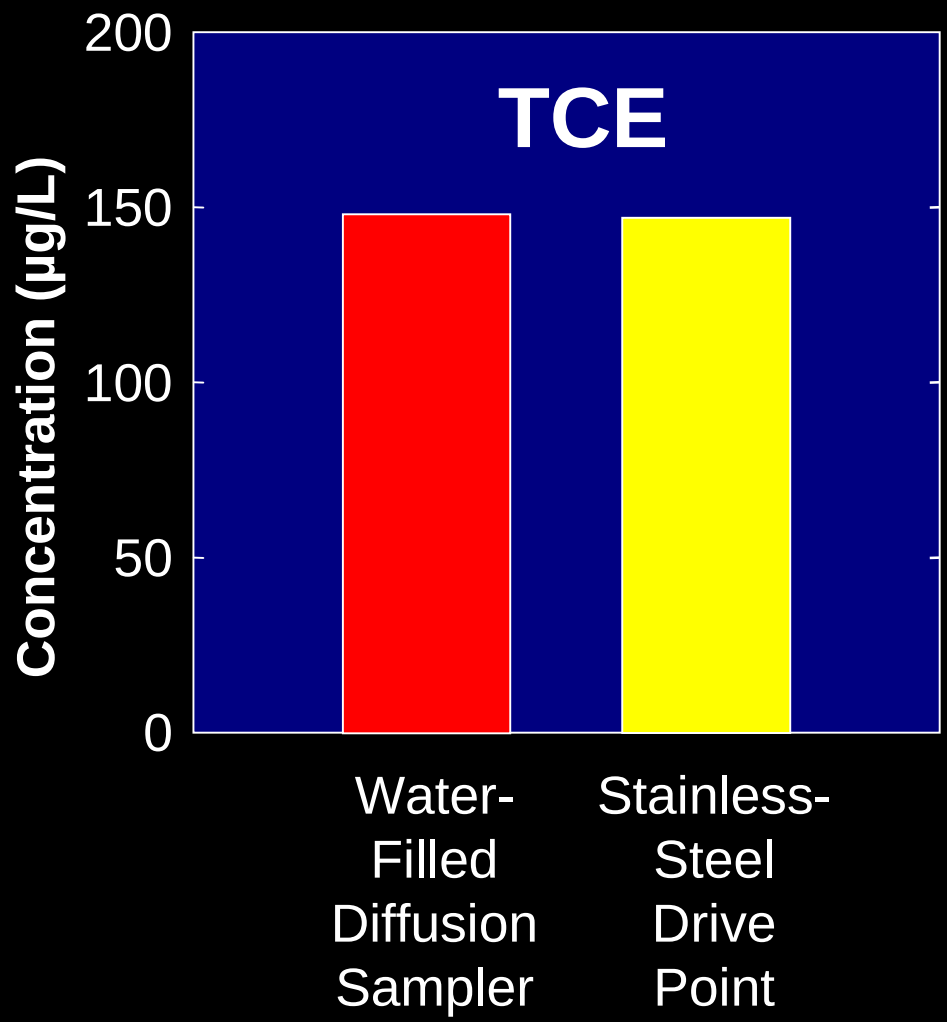
Concentrations in water-to-vapor diffusion samplers beneath the drainage ditch
August 25, 1997, TNX facility, Savannah River Site, SC



Water-Filled Diffusion Samplers

Savannah River Site, SC

- Aqueous concentrations can be obtained beneath stream beds by using water-filled diffusion samplers



Outline

Diffusion Samplers

- Theory (Principles of Operation or Effectiveness)
- Applicability
- Cost
- Regulatory Issues
- Case Histories
- **Advantages and Limitations**
- Summary and Conclusions
- References
- Information Sources and Tech Transfer Tools

Advantages

Diffusion Samplers

- Representative of equilibrium conditions instead of "snap shot" like grab samples
- Ease of use
- Cost
- Minimal field equipment
- Rapid recovery
- Verifiable results (compare to analytical results of sampled vapor or groundwater)

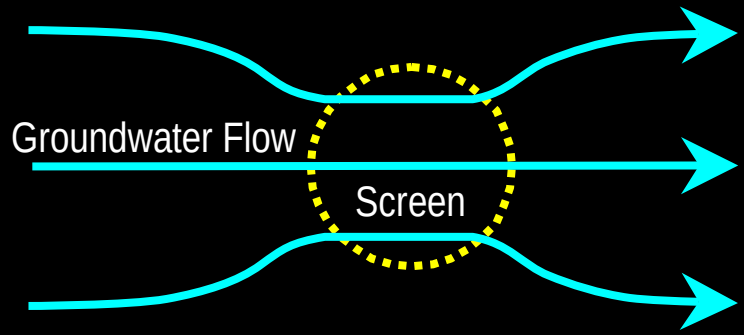
Limitations

Diffusion Samplers

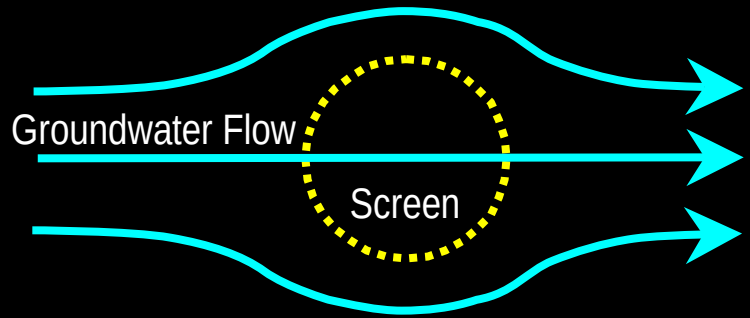
- Regulatory acceptance
- Equilibration period
  (cannot accelerate sample collection time)
- Confirmation studies required
- Not applicable for rapidly changing concentrations
- Not applicable for MTBE, most PAHs, and inorganics
- Well screen must be open for flow

Groundwater Flow Through a Well Screen

Plan View



Aquifer Less Permeable than Well Screen



Aquifer More Permeable than Well Screen

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Summary

Diffusion Samplers

- Results are comparable to traditional methods
- Applicable to a variety of situations
- Inexpensive
- Can sometimes eliminate the need to purge wells

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References

Passive Diffusion Bag References

- Church, P., in press, Evaluation of a diffusion sampling method for determining concentrations of volatile-organic- compounds in ground water, Hanscom Air Force Base, MA, U.S. Geological Survey Water Resources Investigation.
- Harte, P.T, Brayton, M.J., Ives, W., Perkins, S., Brown, C., and Willey, R.E., 2000, Testing and application of diffusion samplers to identify temporal trends in volatile-organic compounds: U.S. Geological Survey Open-File Report 00-196, 88 p.
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- Vroblesky, D.A., and Campbell, T.R., in press, Equilibration times, stability, and compound selectivity of diffusion samplers for collection of ground-water VOC concentrations: Advances in Environmental Research.
- Vroblesky, D.A., and Peters, B.C., in press, Diffusion sampler testing at Naval Air Station North Island, San Diego County, CA, November 1999 to January 2000: U.S. Geological Survey Water-Resources Investigation.

References

Passive Vapor Diffusion Sampler References

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- Savoie, J.G., LeBlanc, D.R., Blackwood, D.S., McCobb, T.D., Rendigs, R.R., and Clifford, Scott, 2000, Delineation of discharge areas of two contaminant plumes by use of diffusion samplers, Johns Pond, Cape Cod, MA, 1998: U.S. Geological Survey Water-Resources Investigations Report 00-4017, 30 p.
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Information Sources and Tech Transfer Tools

Diffusion Samplers

- Document in review (due out in December 2000)
  - Guidance document for use of polyethylene-based diffusion bag samplers to obtain volatile organic compound concentrations in wells
    - Part 1: Assembly, deployment, recovery, data interpretation, quality control and assurance. By D.A. Vroblesky and T.R. Campbell
      - Part 1 Draft available at www.nfesc.navy.mil (NFESC web address)
    - Part 2: Laboratory and field tests. Edited by D.A. Vroblesky
- Detailed table of contents follows in binder

Information Sources and Tech Transfer Tools

Guidance Document: Part 1 Contents

- Part 1: Assembly, deployment, recovery, data interpretation, quality control and assurance. By D.A. Vroblesky and T.R. Campbell
  - Executive Summary
  - Introduction
    - Summary of PDB-Sampler Advantages and Limitations
    - Advantages
    - Limitations
    - Acknowledgments
  - Passive Diffusion Bag Sampler Assembly
  - Diffusion Bag Sampler Deployment
  - Passive Diffusion Bag Sampler Recovery
  - Factors Influencing Interpretation of Diffusion-Sampler Data
  - Quality Control and Assurance
  - Summary
  - References

Information Sources and Tech Transfer Tools

Guidance Document: Part 2 Contents

- Part 2: Laboratory and field tests. Edited by D.A. Vroblesky
  - Chapter A: Equilibration times, compound selectivity, and stability of passive diffusion bag samplers for collection of ground-water volatile organic compound concentrations. By Don A. Vroblesky and Ted R. Campbell
  - Chapter B: Field tests of passive diffusion bag samplers for collection of ground water volatile organic compound concentrations
    - Introduction (Vroblesky)
    - Diffusion sampler evaluation of chlorinated VOCs in ground water (Tunks and others)
    - Diffusion sampler testing at Naval Air Station North Island, San Diego County, CA, November 1999 to January 2000 (Vroblesky and Peters)
    - Investigation of polyethylene passive diffusion samplers for sampling volatile organic compounds in ground water at Davis Global Communication, Sacramento, CA, August 1998 to February 1999 (Vroblesky and others)
    - Diffusion sampler case study: McClellan Air Force Base, CA (McClellan AFB/EM)
    - Field testing of passive diffusion bag samplers for collection of ground water volatile organic compound concentrations at Naval Industrial Reserve Ordnance Plant, Fridley, MN, November 1999 to May 2000 (Vroblesky and Petkewich)
    - Evaluation of a diffusion sampling method for determining concentrations of volatile organic compounds in ground water, Hanscom Air Force Base, MA (Church)
    - Investigation of polyethylene passive diffusion samplers for sampling BTEX compounds in ground water at Fort Stewart, GA, July 1999 (Stoller and others)
    - Testing and application of diffusion samplers to identify temporal trends in volatile-organic compounds (Harte and others)

Information Sources and Tech Transfer Tools

Diffusion Samplers

- TechData Sheet: Release date October 2000
  - Diffusion Membrane Samplers, An Alternative Groundwater Monitoring Tool
  - Available at www.nfesc.navy.mil (NFESC web address)
- Trifold Brochure: Release date October 2000

Information Sources and Tech Transfer Tools

Diffusion Samplers

Vendors

- Columbia Analytical Services
  - 206-824-8933
- Eon Products
  - 800-474-2490

Points of Contact

Diffusion Samplers

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